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# A TEXT-BOOK

OF

# INORGANIC CHEMISTRY

BY

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# PREFACE

In drawing up a systematic course of elementary chemical instruction based upon the periodic classification of the elements, whether it be as a course of lectures, or as a text-book, a number of serious difficulties are at once encountered. These possibly are sufficient to account for the fact, that although twenty-five years have elapsed since Mendelejeff published this natural system of classification, the method has not been generally adopted as the basis of English elementary text-books.

I have endeavoured to obviate many of these difficulties, while still making the periodic system the foundation upon which this little book is based, by dividing the book into three parts. Part I. contains a brief sketch of the fundamental principles and theories upon which the science of modern chemistry is built. Into this portion of the book I have introduced, necessarily in briefest outlines, some of the more recent developments of the science in a physico-chemical direction, of which it is desirable that the student should gain some knowledge, even early in his career.

Part II. consists of the study of the four typical elements, hydrogen, oxygen, nitrogen, and carbon, and of their more important compounds. By dissociating these four elements from their position in the periodic system, and treating them separately, the student is early brought into contact with many of the simpler and more familiar portions of the science. Such subjects as *water*, the *atmosphere*, and *combustion*, to which it is desirable that he should be introduced at an early stage in his studies, are thus brought much more forward than would otherwise be the case.

In Part III. the elements are treated systematically, according to the periodic classification. In this manner, while avoiding a sharp separation of the elements into the two arbitrary classes of metals and non-metals, it has been possible to so far conform to the prevailing methods of instruction, that all those elements which are usually regarded as non-metals (with the two exceptions of boron and silicon) are treated in the earlier portion of the book.

The science of chemistry has of recent years developed and become extended to such a degree, that the difficulty of giving a fairly balanced treatment of the subject, within the limits of a small text-book, is an ever-increasing one, and it necessarily resolves itself into a question of the judicious selection of matter. In making such a selection, I have endeavoured, as far as possible, to keep in view the requirements of students at the present time, without, however, following any examination syllabus.

Acting upon this principle, I have omitted all detailed description of the rare elements and their compounds, confining myself merely to a short mention of them in a few general remarks at the commencement of the various chapters. Although from a purely scientific standpoint, many of these rare substances are of the greatest interest and importance, it must be admitted that they stand quite outside the range of all the customary courses of chemical instruction; and so far as the wants of the ordinary student are concerned, the space which would be occupied by an account of these elements, is more advantageously devoted to such matters as are discussed in the Introductory Outlines. Moreover, it is a matter of common observation, that text-books, even upon the shelves of reference libraries, and which bear unmistakable evidence of much use, are frequently *uncut* in those portions which treat of these elements.

Details of metallurgical processes, also, are out of place in a text-book of chemistry, and must be sought in metallurgical text-books. Only such condensed outlines therefore have been given as are sufficient to explain the chemical changes that are involved in these operations.

The great importance to the student, of himself performing experiments illustrating the preparation and properties of many of the substances treated of in his text-book, cannot well be over-estimated. If he be in attendance upon a course of chemical lectures, opportunity should be given to him for repeating the simpler experiments he may see performed upon the lecture table: if he be not attending lectures, the necessity for this practical work on his part is greater still. Instead of burdening this text-book with specific directions for carrying out such elementary experiments, frequent references have been made to my "Chemical Lecture Experiments," where minute directions are given for carrying out a large number of experiments, many of which may be easily performed, and with the very simplest of apparatus.

Several of the woodcuts have been borrowed from existing modern works, such as Thorpe's "Dictionary of Applied Chemistry," Mendelejeff's "Principles of Chemistry," Ostwald's "Solutions," and others. Care has been taken, however, to exclude all antiquated cuts, and a large number of the illustrations are from original drawings and photographs.

G. S. N.

SOUTH KENSINGTON.

# HINTS TO STUDENTS

FOR the help of students who may use this book at the commencement of their chemical studies, and especially for those who may not be working under the immediate guidance of a teacher, the following hints are given.

Begin by carefully reading the first four chapters (pages 1 to 23). Then pass on to Part II. (page 150), and begin the study of the four typical elements, hydrogen, oxygen, nitrogen, and carbon, and their compounds, in the order in which they are treated. Accompany your reading by performing as many of the experiments referred to as possible, in order that you may become practically familiar with the substances you are studying.

During the time occupied in the study of these four elements and their compounds, again read chapters 1 to 4, and slowly and carefully continue reading Part I., so that by the time Part III. is reached, you may have fairly mastered at least the first thirteen chapters of the Introductory Outlines.

The order in which the elements are treated in Part III. is based upon the Periodic classification, therefore read the short introductory remarks at the commencement of the various chapters, in the light of the table on page 102.

Throughout the book, temperatures are given in degrees of the Centigrade thermometer. 1° Centigrade equals 1.8°

Fahrenheit, and as the zero of the latter scale is 32° below that of the Centigrade, temperatures given in degrees of one scale, are readily translated into degrees of the other, by the simple formula—

$$(n^\circ\text{C.} \times 1.8) + 32 = {}^\circ\text{F.}$$

The abbreviation mm., stands for millimetre; the $\frac{1}{1000}$ part of a metre (1 metre = 39.37079 inches; or roughly, 25 mm. = 1 inch). The abbreviation c.c., signifies cubic centimetre; the $\frac{1}{1000}$ part of a cubic decimetre, or litre (1 litre = 1.76077 pints).

1 gramme (the weight of 1 c.c. of distilled water, taken at its point of maximum density) = 15.43235 English grains.

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# ERRATA.

ge 47, line 9, *for* "one-third" *read* "one-half."
, 71, bottom line, *for* "1.239" *read* "1.293."
, 193, line 33, *for* "loss of four more" *read* "loss of three more."
, 261, top equation, *for* "4Co" *read* "4CO."
, 319, line 22, *for* "analyses" *read* "analysis."
, 413, line 18, *for* "$3Ca_3(PO_4)_2CaCl_2$" *read* "$3Ca_3(PO_4)_2,CaCl_2$."
, 429, 2nd equation, *for* "$H_3PO_3$" *read* "$H_3PO_4$."
, 436, 4th equation, *for* "$2NH_4$" *read* "$2NH_3$."
, 447, line 22, *for* "$H_3AsO_4$" *read* "$H_3AsO_3$."
, 461, 3rd equation, *for* "$3CO + Bi$" *read* "$3CO + 2Bi$."
, 475, line 17, *for* "40" *read* "20."
, 486, line 19, *for* "25" *read* "12."
, 560, line 13, *for* "Dimercuric Ammoninm" *read* "Dimercuric Ammonium."
, 563, 5th and 6th equations, *for* the second = *read* +.
, 577.
, 609.
, 618.
, 623. } In each case, under the heading of the section, *for* "Molecular weight" *read* "Atomic weight."
, 634.
, 639.
, 643.
, 650, index, *for* "Ammonium nitrate, 226" *read* "Ammonium nitrate, 223."

change whereby they become invested with

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# INORGANIC CHEMISTRY

## PART I

## INTRODUCTORY OUTLINES

### CHAPTER I

### *CONSTITUTION OF MATTER*

THE science of chemistry may be described as the study of a certain class of changes which matter is capable of undergoing. Matter is susceptible of a variety of changes, some of which are regarded as *physical* and others as *chemical*. Thus, when a steel knitting-needle is rubbed upon a magnet, the needle undergoes a change, by virtue of which it becomes endowed with the power of attracting to itself iron filings or nails: and when an ordinary lucifer match is rubbed upon a match-box, the match undergoes a change, resulting in the production of flame. In the first case the change is said to be a *physical* one, while the ignition and combustion of the match is a *chemical* change.

When a fragment of ice is gently warmed, it is changed from a hard, brittle solid to a mobile, transparent liquid; and when white of egg is gently heated, it changes from a transparent, colourless liquid to an opaque white solid. These changes, which appear at first sight to be of a similar order, are in reality essentially different in their nature: the transformation of solid ice into liquid water is a *physical* change, the coagulation of albumen is a *chemical* change.

Again, when certain substances (such as the materials which constitute the so-called *luminous paint*) are exposed to a bright light, they undergo a change whereby they become invested with

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the power to emit a feeble light when seen in the dark. A stick of phosphorus also emits a very similar light when seen in the dark. The glowing of these materials under these circumstances might readily be regarded as the result of the same kind of change in both cases, but in reality the luminosity of the phosphorus is due to a *chemical* change taking place upon the surface of that substance, while the emission of light from the luminous paint is a purely *physical* phenomenon.

The two sciences, chemistry and physics, are so closely related and interdependent upon each other, that no sharp distinction or line of separation between them is possible. Every *chemical* change that takes place is attended by some *physical* change, and it often happens that this accompanying physical change forms the only indication of the chemical change that has taken place. In certain important points, however, a chemical change is very different from one that is purely physical: in the latter case no material alteration in the essential nature of the substance takes place. This will be seen in the examples quoted. The steel needle remains unaltered in its essence, although by magnetisation it has acquired a new property, a property which it again loses, and which can be again and again imparted to it. The match, on the other hand, when ignited has undergone a material and permanent change: the combustible substance is now no longer combustible, neither will it ever return to its original state. The solid water, in being transformed to liquid water, has not undergone any vital change: in essence it is the same substance merely endowed with a new property of liquidity, a property which it loses again when cooled, and which can be again and again imparted to it: on the other hand, the coagulated albumen has undergone a complete and lasting change, and never returns to its original condition.

In the same way, the luminous paint gradually ceases to emit light, and returns to its original state; it may be exposed to the influence of light, when it once more acquires the property of phosphorescence, and this change may be brought about indefinitely, without altering the intrinsic nature of the substance. The glowing phosphorus, on the other hand, is gradually changed into a white substance, which escapes from it as a smoke or fume; in the act of glowing the phosphorus is undergoing a process of slow burning, and if allowed to remain will continue glowing and burning until the whole of it has disappeared in the form of smoke.

**The Constitution of Matter. Molecules.**—Matter is regarded by the chemist and physicist as being composed of aggregations of minute particles: every substance, whether it be solid, liquid, or gaseous, presents the appearance to his mind of a vast number of extremely minute particles. To these particles the name molecules ("little masses") has been given. The particles or molecules of any particular substance are all alike: thus in sulphur the molecules are all of one kind, while in water they are all of another kind; the properties associated with sulphur are the properties of the individual sulphur molecules, while those belonging to water are the properties of the molecules of that substance. All matter, therefore, is to be conceived as having what may be called a *grained* structure. The actual sizes of molecules is a matter which has not yet been determined with exactness; they are orders of magnitude which are as difficult for the mind to grasp on account of their minuteness, as many astronomical measurements are by reason of their vastness. It is certain that their size is less than half a single *wave-length* of light,* and that therefore they are beyond the visual limits of the microscope. Some general idea of their order of magnitude may be gathered from Lord Kelvin's calculation, that if a single drop of water were magnified to the size of the earth, each molecule being proportionately enlarged, the grained appearance which the mass would present would probably be finer than that of a heap of cricket-balls, but coarser than a heap of small shot.

It will be evident, therefore, that in the strictest sense matter is not *homogeneous:* a fragment of ice or a drop of water consists of an aggregation of a certain number of molecules, between which there exist certain interspaces. When the fragment of ice is heated, the spaces between the molecules are enlarged, and the solid passes into the liquid state; and when water is still further heated, and converted into water vapour, or steam, the molecules are still more thrust asunder, and the inter-molecular spaces are still further increased.

The forces which similar molecules exert upon each other are regarded as *physical*, in contradistinction to *chemical*. These forces are either *attractive* in their nature, or *repellent*. When the attractive forces are in the ascendency, the molecules are drawn more or less closely together, and the substance assumes the solid state. If the repellent forces have the upper hand the material takes the gaseous condition, while the liquid state may be regarded as resulting from a certain balance of these opposite forces. Changes which matter undergoes by the action of these forces are *physical* changes, they do not affect the inherent nature and properties of the substance, which properties, as already stated, reside in the molecules themselves.

---

* The wave-length of the blue ray (G) = $0.000_4311$ millimetre, or 0·0000169 inch.

In each of the three states of matter, viz., solid, liquid, or gaseous, the molecules are conceived as being in a state of motion; they are regarded as executing some vibratory movement within the spaces that divide them. In the solid state this movement is the most restricted for the reason that the intermolecular spaces are in this case the smallest. In the gaseous condition the *amplitude of vibration* of the molecules is very greatly increased; for the attractive forces being at a minimum, and the intermolecular spaces being greatest, the molecules have a further distance to travel before they strike one another.

Such changes in matter, which are merely the result of alterations in the motions of the molecules, are likewise purely *physical changes.*

Molecules may be defined as *the smallest particles of matter which can exist in the free state;* or as *the smallest weight of matter in which the original properties of the matter are retained.*

**Atoms.**—It is the belief of chemists that most molecules are possessed of a *structure.* That is to say, they are not simple, single, indivisible masses, but themselves consist of aggregations of still smaller particles, which are held together by the operations of some other force. These particles of which molecules are composed are termed atoms, and the force which holds them together is called chemical affinity, or chemical attraction. To the mind of the chemist, such molecules are little systems, consisting of a number of atoms which are attracted to each other by this particular force; in the ordinary movements of the molecule, the system moves about as a whole. In this respect it bears some analogy, on an infinitely minute scale, to a solar system. The atoms of a molecule are regarded as in a state of motion as respects one another, possibly revolving about one another, while the entire system, or molecule, at the same time performs its independent movements, just as in a solar system the various members perform various movements towards each other, while at the same time the whole system travels upon its prescribed orbit. In the case of the heavenly bodies the force which regulates the movements of the individual members of the system amongst themselves, is the same force that controls the motion of the united system, namely, gravitation. What is the precise relation, or difference, if any, between the forces which control the movements of molecules, and those which operate between the atoms of the molecule, is not known; but as the effects produced are different the latter force is distinguished by the name of chemical affinity.

Any change which matter undergoes, in which the integrity of the molecules is not destroyed, is regarded as a physical change; while any change which arises from an alteration in the structure of the molecule is a chemical change. For example, the molecules of water consist of three separate atoms, one of oxygen and two of hydrogen; any change which water can be made to undergo, in which these three atoms still remain associated together as the molecule, is a physical change. The water may be converted into ice, or it may be changed into steam; but these alterations still leave the molecules intact, the three atoms still remain united as an unbroken system, and so long as this is the case chemical change has not taken place.

Suppose now the molecules of water are heated to a much higher temperature than that which is necessary to convert the water into steam, by passing electric sparks through the steam. It will then be found that a very different kind of change has come over the substance. The steam, after being so heated, no longer condenses to water again when cooled; it has been changed into a gas which can be bubbled through water and collected in an inverted vessel filled with water standing in a pneumatic trough, and if a flame be applied to this gas a sharp explosion takes place. The change in this case is a chemical change, for the integrity of the molecules of water has been destroyed. The two atoms of hydrogen have become detached from the oxygen atom, and the original triune structure of the system is destroyed.

Atoms are therefore defined as *the smallest particles of matter which can take part in a chemical change.*

# CHAPTER II

## *ELEMENTS AND COMPOUNDS*

THERE are certain molecules in which all the atoms present are of the same kind, and there are other molecules which are composed of atoms which differ from one another. Thus, in the substance sulphur, all the atoms composing the molecules are alike; while in water, as already mentioned, there are two distinct kinds of atoms in the molecule. Matter, therefore, is divided into two classes, according as to whether its molecules are composed of similar or of dissimilar atoms. Molecules consisting of atoms of the same kind are termed *elementary molecules*, and substances whose molecules are so constituted are known as elements; molecules, on the other hand, which contain dissimilar elements are called *compound molecules*, and substances whose molecules are thus composed are distinguished as compounds.

Sulphur, therefore, is an *element*, and water is a *compound*. It will be evident that in the case of elementary molecules, whatever processes they may be subjected to, only one kind of matter can be obtained from them; while in the case of compounds, the molecules consisting of dissimilar atoms, as many different kinds of matter can be obtained as there are different atoms present. By appropriate means the atoms of hydrogen and oxygen in water molecules can be separated, and two totally different kinds of matter, namely, hydrogen and oxygen, can be obtained from this compound.

At the present time there are about seventy substances known to chemists which are believed to be elements. In the history of the science it has frequently happened that substances which were considered to be elements have proved, when subjected to new methods of investigation, to be in reality compound bodies: thus, prior to the year 1783, water was thought to be an elementary substance, it was indeed regarded as the very type of an element, until Cavendish and Lavoisier proved that it was composed of two entirely different kinds of matter. In the year 1807, Sir Humphrey Davy showed that the substances known as potash and soda, which were believed to be elements, were in reality compound bodies, and he succeeded in separating the constituent atoms in the molecules of these substances, and in obtaining from them two essentially different kinds of matter. It is therefore quite possible, perhaps even probable, that some at least of the forms of matter which are now held to be elements, may yet prove to be compound bodies.

The number of compounds is practically infinite.

The elements are very unequally distributed in nature, and are of very different degrees of importance to mankind. Some are absolutely essential to life as it is constituted, while others might be blotted out of creation without, so far as is known, their absence being appreciated. The following thirty elements include all the most important (for the complete list see page 21):—

Aluminium.
Antimony.
Arsenic.
Bismuth.
Bromine.
Calcium.
Carbon.
Chlorine.
Copper.
Fluorine.
Gold.
Hydrogen.
Iodine.
Iron.
Lead.
Magnesium.
Manganese.
Mercury.
Nickel.
Nitrogen.
Oxygen.
Phosphorus.
Platinum.
Potassium.
Silicon.
Silver.
Sodium.
Sulphur.
Tin.
Zinc.

On account of certain properties common to a large number of the elements, and more or less absent in others, properties which are for the most part physical in character, the elements are divided into two classes, known as *metals* and *non-metals*. The metals generally are opaque, and their smoothed surfaces reflect light to a high degree, thus giving them the appearance known as *metallic lustre*. They also conduct heat and electricity. Gold, silver, copper, iron, are metals; sulphur, bromine, oxygen, phosphorus, are non-metals. These two classes, however, gradually merge into one another, and certain elements are sometimes placed in one division and sometimes in the other, depending upon whether the distinction is based more upon their physical or their chemical properties: thus, the element arsenic possesses many of the physical properties of a metal, but in its chemical relations it is more allied to the non-metals: such elements as these are often distinguished by the name *metalloids*. By general consent the following fifteen elements are regarded as including all the non-metals and metalloids:—

Arsenic.
Boron.
Bromine.
Carbon.
Chlorine.
Fluorine.
Hydrogen.
Iodine.
Nitrogen.
Oxygen.
Phosphorus.
Selenium.
Silicon.
Sulphur.
Tellurium.

The number of atoms which compose the various elementary molecules is not the same in all cases: thus in the elements sodium, potassium, cadmium, mercury, and zinc, the molecules consist of only one atom. The molecules of these substances are single particles of matter. The terms *molecule* and *atom*, therefore, as applied to these elements, are synonymous. Such molecules as these are called *mono-atomic* molecules. In many cases elementary molecules consist of two atoms; such is the case with the elements hydrogen, bromine, chlorine, oxygen, nitrogen, and others. Elementary molecules of this twin or dual nature are known as *di-atomic* molecules. Only one instance is known in which an elementary molecule consists of a trio of atoms, namely, the molecule of ozone, which is an aggregation of three oxygen atoms. This molecule is said to be *tri-atomic*. In two cases, namely, arsenic and phosphorus, the molecules are composed of a quartette of atoms, and these elements, therefore, are said to form *tetr-atomic* molecules. In a large number of instances the atomic constitution of the molecule of the elements is not known. These terms, *mono-atomic*, *di-atomic*, &c., are applied exclusively to molecules of *elements*, and are not used in reference to compounds, where the molecules are composed of dissimilar atoms.

**Mechanical Mixtures.**—When molecules of different kinds of matter are brought together, one of two results may follow: either they will merely mingle together without losing their identity, that is to say, the atoms composing the individual molecules will still remain associated together as before, or the atoms in the molecules of one kind will attach themselves to certain atoms present in molecules of another kind to form still different molecules; in other words, there will be a redistribution of the atoms, whereby different systems or molecules are produced.

In the first case the result is said to be a simple or mechanical mixture, in the second it is the formation of a chemical compound.

In a simple *mixture*, the ingredients can be again separated by purely mechanical methods; and as the properties of a substance are the properties of the molecules of that substance, it follows that if the integrity of the molecules is not broken, the properties of a mechanical mixture will be those of the ingredients. For example, oxygen is a colourless gas without taste or smell; hydrogen also is a colourless gas without taste or smell: when these two gases are mixed together, the mixture is gaseous, is colourless, and tasteless, and, being only a mixture, the molecules of one gas can be readily sifted away from the other.

Again, charcoal is a black solid, insoluble in water; sulphur is a yellow solid, also insoluble in water; nitre is a white solid, readily dissolved by water: when these three substances are finely powdered and mixed together, the result is a mechanical mixture, which is solid, and which is dark grey or nearly black in colour. If this mixture be placed in water, the nitre is dissolved away and the charcoal and sulphur are left.

When, however, the integrity of the molecules is disturbed, when, by bringing together molecules of different substances, a rearrangement of the atoms takes place, resulting in the formation of new molecules, then it is said that chemical action has taken place.

Chemical action, therefore, always results in the formation of new molecules,—new molecules which are endowed with their own special properties, differing often in the most remarkable and quite inexplicable manner from those of the original molecules. One or two examples may be quoted in order to illustrate this extraordinary modifying effect of chemical action. The two colourless gases, oxygen and hydrogen, when simply mixed together, give rise, as already mentioned, to a colourless, gaseous mixture, in which the dual molecules of hydrogen and the similarly constituted oxygen molecules move about freely amongst each other. By suitable means chemical action may be made to take place between these two elements, whereby a complete rearrangement of the atoms takes place, resulting in the formation of molecules of water—molecules in which, as has been already mentioned, one atom of oxygen is associated with two atoms of hydrogen. The product of the chemical action is therefore water, while both the forms of matter of which it is composed are gaseous.

The air we breathe, and which is necessary to life, consists of a simple mixture of two colourless gases, viz., oxygen and nitrogen: when chemical action takes place between these substances, a brown-coloured gas is produced in which no animal or vegetable life could exist for many minutes, on account of its suffocating nature.

Common salt, which is a white solid substance, and not only harmless but even a necessary article of food, contains two atoms in its molecules—one an atom of chlorine, which is a yellow gas, intensely suffocating and poisonous; and the other an atom of sodium, a soft, silver-like metal, which takes fire in contact with water.

Why it is that a molecule, consisting of an atom of chlorine and an atom of sodium held together by chemical affinity, should be endowed with properties so totally different from those of the contained elements, is altogether unknown; and, similarly, it is quite impossible to predicate from the properties of any compound what are the particular elements of which it is composed. Thus, sugar is a white crystalline solid, soluble in water, and possessing a sweet taste, but no one would have ventured to predict that the molecules of this substance were composed of atoms of *carbon* (*i.e.*, charcoal), a black, tasteless, insoluble solid; *hydrogen*, a colourless, tasteless gas; and *oxygen*, another colourless, tasteless gas.

**Chemical Affinity.**—When molecules, consisting of two atoms, say A B, come in contact with molecules consisting of other two atoms, C D, and a chemical change takes place resulting in the formation of new molecules, A C and B D; the question naturally arises, Why does the atom A leave the atom B and attach itself to C? In other words, what determines the rearrangement of the atoms into new molecules?

At present no exact answer can be given to this question. Chemists express the fact by saying that the chemical affinity existing between A and C is greater than that exerted by B upon A. This remarkable selective power possessed by the atoms of different elements lies at the root of all chemical phenomena, and it differs between the various elements to an extraordinary degree.

For example, the atom of chlorine possesses a very powerful chemical affinity for the atom of hydrogen: when hydrogen molecules, which consist of two atoms, are mixed with chlorine molecules, which are also aggregations of two atoms, at first a simple mechanical mixture is obtained, the two different kinds of molecules move amongst each other without undergoing change. On very small provocation, however, the affinity of the hydrogen atoms for the chlorine atoms can be caused to exert itself; by merely momentarily exposing the mixture to sunlight a complete redistribution of the atoms suddenly takes place with explosive violence and new molecules are formed, each containing one atom of hydrogen and one atom of chlorine.

Again, an atom of nitrogen is capable of associating itself in chemical union with three atoms of the element chlorine, forming a compound whose molecules therefore contain four atoms. The chemical affinity between the atoms of chlorine and nitrogen is so feeble, the system is, so to speak, in a state of such unstable equilibrium, that the very slightest causes are sufficient to instantly separate the atoms in the most violently explosive manner, and so break up the compound molecule into separate molecules of chlorine and nitrogen. In this case the affinity between one chlorine atom and another chlorine atom is greater than that between chlorine and nitrogen, consequently the redistribution that results is of the opposite order to that of the former example.

As a rule, those elements which the more closely resemble each other in their chemical habits have the least affinity for each other, while the greatest affinity usually exists between those which are most dissimilar.

**Chemical Action.**—The actual process of redistribution of the atoms that takes place when molecules of different kinds of matter are brought together, is called *chemical action*. In many cases chemical action takes place when the substances are merely brought together, while in others it is necessary to expose the bodies to the influence of some external energy: thus chemical action is brought about in a great number of instances by the application of heat to the substances. In some cases the influence of light has the effect of causing chemical action to take place: for example, when the gases chlorine and hydrogen are mingled together, no chemical action takes place in the dark, but on exposing the mixture to light the hydrogen and chlorine combine, and form the compound hydrochloric acid. It is upon the effect of light in causing chemical action to take place that the art of photography depends.

Chemical action may sometimes be induced by the influence of pressure: thus when the two gases, hydrochloric acid and phosphoretted hydrogen, are subjected to increased pressure, they combine together to form a crystalline solid compound known as phosphonium chloride. In the same way, by very great mechanical pressure, a mixture of powdered lead and sulphur can be caused to combine together, when they form the compound, lead sulphide. There are also a number of chemical actions that are only able to proceed in the presence of small quantities (often *extremely* small) of a third substance, which itself remains unchanged at the conclusion of the action. These cases are generally included under the name of *catalytic* actions: in some of them the *modus operandi* of the third substance can be traced (see Oxygen, Modes of Formation; also Chlorine, Deacon's Process), while in others it is not understood; thus it is found that a number of chemical actions are quite unable to take place if the materials are *absolutely* dry: for example, the element chlorine has a powerful affinity for the metal sodium, and when these substances are brought together under ordinary conditions, chemical action instantly takes place, and the compound known as sodium chloride (common salt) is produced. If, however, every trace of moisture be perfectly removed from both the sodium and the chlorine, no action between these elements takes place when they are brought together, and so long as they remain in this state of perfect dryness no chemical change takes place. The admission into the mixture of the minutest trace of the vapour of water, however, at once induces chemical action between the chlorine and the sodium, but the exact part that the trace of moisture plays in producing this effect, is not known with certainty. (See also foot-note, page 86.)

A few interesting cases are known in which chemical action is brought about by the vibration caused by a loud sound or note: for example, the molecules of the gas acetylene consist of two atoms of carbon associated with two of hydrogen; when a quantity of this gas is exposed to the report produced by the detonation of mercury fulminate, the mere shock of the explosion causes a redistribution of the atoms whereby solid carbon is deposited and hydrogen set free. We may suppose that the particular vibration produced by the detonation of the fulminate exercises a disturbing effect upon the motions of the atoms constituting the molecules of acetylene, and thereby causes them to swing beyond the sphere of their mutual attractions, and thus the system undergoes disruption and rearrangement.

All known instances of chemical action can be referred to one of three modes, in which the rearrangement of the atoms can take place.

(1.) *By the direct union of two molecules to form a more complex molecule.* Thus, if $\mathrm{CO}$ and $\mathrm{ClCl}$ represent two molecules between which chemical action takes place according to this mode, they unite to form a molecule containing the four atoms $\mathrm{COClCl}$.

(2.) *By an exchange of atoms taking place between different molecules.* In its simplest form this is illustrated in the action of one element upon another to form a compound. Thus, if $\mathrm{HH}$ and $\mathrm{ClCl}$ stand for two elementary molecules between which chemical action takes place, the result is the formation of the two molecules $\mathrm{HCl}$ $\mathrm{HCl}$. Such a process as this, in which a compound substance is produced directly from the elements which compose it, is termed *synthesis*.

The same mode of chemical action may also be exemplified by the exact opposite to this process, namely, the resolution of a compound into its constituent elements. Thus, if $\mathrm{OHH}$ $\mathrm{OHH}$ represent two molecules of the same compound, when chemical action takes place it will result in the formation of the three elementary molecules $\mathrm{OO}$, $\mathrm{HH}$, and $\mathrm{HH}$. Such a process as this, in which a compound is resolved into its elements, is known as *analysis*.

(3.) *By a rearrangement of the atoms contained in a molecule.* There are a number of instances of chemical change, in which the molecules of the substance do not undergo any alteration in their *composition*—that is to say, no atoms leave the molecule, nor are any added to it. The molecule still consists of the same atoms after the change as it did before, but the chemical action has caused them to assume new relative positions, or different relative motions with respect to each other. For example, the substances known to chemists as *ammonium cyanate* and *urea* are two totally different and distinct kinds of matter. These molecules, however, each contain the same atoms and in the same number; they each consist of aggregations of one atom of carbon, one atom of oxygen, two atoms of nitrogen, and four atoms of hydrogen. When ammonium cyanate is gently warmed, the eight atoms composing the molecules undergo this process of rearrangement, and the substance is changed into urea.

# CHAPTER III

## *CHEMICAL NOMENCLATURE*

THE names which have been given to the various elementary forms of matter are not based upon any scientific system. The names of some have their origin in mythology. Others have received names which are indicative of some characteristic property, while those of several bear reference to some special circumstance connected with their discovery. It has been the custom in modern times, to distinguish metals from non-metals by applying to the former names ending in the letters *um*, and consequently such metals as are of more recent discovery all have names with this termination. The common metals, however, which have been known since earlier times, such as gold silver, tin, and copper, keep their old names. The two elements selenium and tellurium were at the time of their discovery thought to be metals, and they consequently received names with the terminal *um;* these substances strongly resemble metals in many of their physical properties, but in their chemical relations they are so closely similar to the non-metal sulphur, that they are by general consent classed among the non-metals; they are examples of those elements which are distinguished as metalloids. On this account selenium is by some chemists termed *selenion*.

In naming chemical compounds, the chemist endeavours that the names employed shall not only serve to identify the substances, but shall as far as possible indicate their composition. The simplest chemical compounds are those composed of only two different elements; such are spoken of as *binary compounds*, and their names are made up of the names of the two elements composing them, thus—

The compound formed by the chemical union of—

| | | | | |
|---|---|---|---|---|
| Hydrogen | with | sulphur | is called | hydrogen sulphide. |
| Sodium | ,, | chlorine | ,, | sodium chloride. |
| Copper | ,, | oxygen | ,, | copper oxide. |
| Calcium | ,, | fluorine | ,, | calcium fluoride. |
| Potassium | ,, | iodine | ,, | potassium iodide. |

It continually happens, however, that the same two elements combine together in more than one proportion, giving rise to as many different compounds, in which case it becomes necessary to so modify the names that each of the compounds may be distinguished. This is accomplished by the use of certain terminal letters, or of certain prefixes; for example, the element phosphorus combines with chlorine in two proportions, forming two different compounds—in one the molecules contain one atom of phosphorus united to three atoms of chlorine, in the other the molecules consist of one atom of phosphorus associated with five of chlorine. These two compounds may be distinguished in the following ways:—

1 atom of phosphorus with 3 atoms of chlorine forms phosphor*ous* chloride.
1 ,, ,, ,, 5 ,, ,, ,, phosphor*ic* chloride.

or—

1 atom of phosphorus with 3 atoms of chlorine forms phosphorus *tri*chloride.
1 ,, ,, ,, 5 ,, ,, ,, phosphorus *penta*chloride.

The latter method of distinction is the more general, thus—

1 atom of sulphur with 2 atoms of oxygen forms sulphur dioxide.
1 ,, ,, ,, 3 ,, ,, ,, sulphur trioxide.
1 atom of carbon with 1 atom of oxygen forms carbon monoxide.
1 ,, ,, ,, 2 atoms ,, ,, carbon dioxide.

Occasionally the prefixes *sub* and *proto* are employed to denote these differences of composition, but their use is more limited, and is becoming out of vogue. When more than two compounds are formed by the union of the same two elements, the additional prefixes *hypo*, under, and *per*, over, are sometimes used.

In a considerable number of instances the systematic names of familiar compounds give way to the vulgar or common names by which they are known, thus—

| Common names | Systematic names |
|---|---|
| Ammonia . . . | Hydrogen nitride |
| Hydrochloric acid . | Hydrogen chloride |
| Sulphuretted hydrogen . | Hydrogen sulphide |
| Water . . . . | Hydrogen monoxide |

Binary compounds that are formed by the union of elements with oxygen are called the *oxides* of those elements. Certain of these oxides are capable of entering into combination with water, giving rise to substances known as *acids*: such oxides are distinguished as *acid-forming oxides*, or *acidic* oxides. They are also sometimes termed *anhydrides*. All the non-metallic elements, except hydrogen, form oxides of this order, and the acids derived from them are known as the oxy-acids.

Certain other oxides also unite with water, but give rise to compounds known as *hydroxides*. When such oxides, which are all derived from the metallic elements, are brought into contact with acids, chemical union takes place, and a compound termed a *salt* is formed. Such oxides are distinguished as *salt-forming*, or *basic* oxides. There are also oxides which are neither *acidic* nor *basic*. The names of oxy-acids are derived from the name of the particular oxide from which they are formed, thus—

Carbon dioxide gives carbonic acid.
Silicon dioxide „ silicic acid.

When the same element forms two acid-forming oxides, the terminals *ic* and *ous* are applied to the acids to denote respectively the one with the greater and the less proportion of oxygen, thus—

Sulphur *tri*oxide gives sulphur*ic* acid.
Sulphur *di*oxide gives sulphur*ous* acid.
Nitrogen *pent*oxide gives nitr*ic* acid.
Nitrogen *tri*oxide gives nitr*ous* acid.

When more than two such acids are known, the additional prefixes *hypo* or *per* are made use of. Thus *per*sulphuric acid denotes an acid containing the highest quantity of oxygen, while *hypo*nitric acid stands for an acid containing less oxygen than is present in nitrous acid.

There is a class of binary compounds formed by the combination of a large number of the elements with sulphur; these are known as *sulphides*. Certain of these sulphides are also capable of forming acids which are analogous in their constitution to oxy-acids, but in which the oxygen atoms are substituted by atoms of sulphur. These acids are known as *thio* acids (sometimes *sulpho* acids), and the same system of nomenclature is adopted to distinguish these: thus we have thio-arseni*ous* acid, thio-arsen*ic* acid, denoting respectively the acid with the smaller and the larger proportion of sulphur.

It was at one time believed that *all acids* contained oxygen, that indeed this *element was essential to* an acid. The name *oxygen* indicates this belief, the word signifying "the acid-producer." This view is now seen to have been incorrect, for many acids are known in which oxygen is not one of the constituents. Thus the elements fluorine, chlorine, bromine, and iodine, which constitute the so-called Halogen group of elements, each combine with hydrogen, giving rise respectively to hydrofluoric, hydrochloric, hydriodic, and hydrobromic acids.

All known acids contain hydrogen as one of their constituents.

As already stated, when chemical action takes place between an acid and a base, a *salt* is formed. Oxy-acids in this way give rise to oxy-salts, thio-acids to thio-salts, and halogen acids to haloid salts.

The latter salts being *binary* compounds, their names are given according to the system already explained, such for example as calcium fluoride, sodium chloride, potassium bromide, silver iodide.

In the case of the oxy-salts and thio-salts, the names are made up from the names of the acid and of the metal contained in the base, with the addition of certain distinctive suffixes: thus if the acid be one whose name carries the terminal *ous* its salts will be distinguished by the suffix *ite*, while the names of the salts derived from acids whose names end in *ic* are terminated by the letters *ate*.

Nitr*ous* acid and potassium oxide give potassium nitr*ite*.
Sulphur*ous* acid „ „ „ sulph*ite*.
Nitr*ic* acid „ „ „ nitr*ate*.
Sulphur*ic* acid „ „ „ sulph*ate*.

The formation of a salt by the action of an acid upon a base, is due to the redistribution of the atoms composing the molecules of the two compounds, in such a manner that some or all of the hydrogen atoms in the acid molecules, exchange places with certain metallic atoms from the molecules of the base. Acids which contain only one atom of hydrogen so capable of becoming exchanged for a metal, are termed *mono-basic* acids; those with two, three, or four such hydrogen atoms are distinguished respectively as *di-basic*, *tri-basic*, and *tetra-basic* acids.

If the whole of the displaceable hydrogen in an acid becomes replaced by the base, the salt formed is known as a *normal* salt. On the other hand, when only a portion of the hydrogen atoms is displaced by the base, the salt is distinguished as an *acid* salt. Thus sulphuric acid contains two atoms of hydrogen in its *molecule* (associated with one of sulphur and four of oxygen); if both the hydrogen atoms are exchanged for potassium, the salt obtained is *normal potassium sulphate*, and when only one is so replaced the salt is known as *acid potassium sulphate*. By the term *acid salt*, therefore, must be understood a salt in which one or more of the hydrogen atoms of the original acid are still left in the molecule.*

A third class of salts is formed by the association of one or more molecules of normal salt, with one or more additional molecules of the base: these are known as *basic* salts. Thus, carbonic acid and the base lead oxide, form such a salt known as *basic lead carbonate*.

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* Some chemists prefer to regard the acids themselves as the hydrogen salts; accordingly they apply to nitric acid, sulphuric acid, nitrous acid, sulphurous acid, &c., the names hydrogen nitrate, hydrogen sulphate, hydrogen nitrite, hydrogen sulphite, &c., respectively.

# CHAPTER IV

## *CHEMICAL SYMBOLS*

CHEMISTS are agreed in adopting certain symbols to denote the atoms of the various elementary forms of matter. The table opposite contains the names of the elements at present recognised, and in the second column are given the symbols which are employed to represent their atoms. The names of the rare elements are printed in italics.

In a number of instances the atomic symbol is the initial letter of the ordinary name of the element: thus Boron, B; Carbon, C; Fluorine, F; Hydrogen, H; Oxygen, O; Sulphur, S.

When more than one element has the same initial, either the first two letters of the name, or the first and another that is prominently heard in pronouncing the word are employed, as Bromine, Br; Cobalt, Co; Chlorine, Cl; Platinum, Pt. In some cases letters taken from the Latin names for the elements are used, such as Antimony (*Stibium*), Sb; Gold (*Aurum*), Au; Silver (*Argentum*), Ag; Lead (*Plumbum*), Pb; and Iron (*Ferrum*), Fe.

These symbols are not intended to be employed as mere shorthand signs, to be substituted as abbreviations for the full names of the elements, but in every case they denote one atom of the element. The symbol H stands for one atom of hydrogen, the symbol O stands for one atom of oxygen; Cl means one atom of chlorine, and Ag represents one atom of silver. No other use of these symbols is legitimate.

It has been already mentioned (page 8) that the molecules of the different elements are composed of different numbers of atoms; for example, the molecule of hydrogen consists of two atoms, and ordinary oxygen also forms diatomic molecules. These facts are expressed in chemical notation by the use of small numerals placed immediately after the symbol of the atom, thus $H_2$ denotes a molecule of hydrogen, $O_2$ a molecule of oxygen. The molecule of ozone consists of an aggregation of three atoms of oxygen, and is

|  |  | Atomic Weights. |  |  |  | Atomic Weights. |  |
|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| Name. | Atomic Symbols. | Approximate Values. | More Exact* Values. | Name. | Atomic Symbols. | Approximate Values. | More Exact* Values. |
| Aluminium . . . | Al | 27 | 27.04 | *Molybdenum* . . | Mo | 96 | 95.9 |
| Antimony (*Stibium*) | Sb | 120 | 119.6 | Nickel . . . . | Ni | 59 | 58.6 |
| Arsenic . . . . | As | 75 | 74.9 | *Niobium* . . . | Nb | 93·7 | . . |
| Barium . . . . | Ba | 137 | 136.86 | Nitrogen . . . | N | 14 | 14.01 |
| *Beryllium* . . . | Be | 9 | 9.08 | *Osmium*. . . . | Os | 191 | ... |
| Bismuth . . . | Bi | 207·5 | ... | Oxygen . . . . | O | 16 | 15.96 |
| Boron . . . . | B | 11 | 10.9 | Palladium . . . | Pd | 106 | 106.2 |
| Bromine . . . | Br | 80 | 79.76 | Phosphorus . . | P | 31 | 30.96 |
| Cadmium . . . | Cd | 112 | 111.7 | Platinum . . . | Pt | 195 | 194.3 |
| *Caesium* . . . | Cs | 133 | 132.7 | Potassium (*Kalium*) . . . | K | 39 | 39.03 |
| Calcium . . . | Ca | 40 | 39.91 |  |  |  |  |
| Carbon . . . . | C | 12 | 11.97 | *Rhodium* . . . | Rh | 104 | 104.1 |
| *Cerium* . . . . | Ce | 141·2 | ... | *Rubidium* . . . | Rb | 85 | 85.2 |
| Chlorine . . . | Cl | 35·5 | 35.37 | *Ruthenium*. . . | Ru | 103·5 | ... |
| Chromium . . . | Cr | 52 | 52.45 | *Samarium* . . . | Sm | 150 | ... |
| Cobalt . . . . | Co | 59 | 58.6 | *Scandium* . . . | Sc | 44 | 43.97 |
| Copper (*Cuprum*). | Cu | 63 | 63.18 | Selenium . . . | Se | 79 | 78.87 |
| *Didymium* . . . | Di | 145 | ... | Silicon . . . . | Si | 28 | 28.3 |
| *Erbium* . . . . | Er | 166 | ... | Silver (*Argentum*) | Ag | 108 | 107.66 |
| Fluorine. . . . | F | 19 | 19.06 | Sodium (*Natrium*) | Na | 23 | 22.995 |
| *Gallium*. . . . | Ga | 70 | 69.86 | Strontium . . . | Sr | 87·3 | ... |
| *Germanium* . . | Ge | 72 | ... | Sulphur. . . . | S | 32 | 31.98 |
| Gold (*Aurum*) . | Au | 197 | 196.8 | *Tantalum* . . . | Ta | 182 | ... |
| Hydrogen . . . | H | 1 | ... | Tellurium . . . | Te | 125 | ... |
| *Indium* . . . . | In | 113 | 113.4 | Thallium . . . | Tl | 203·7 | ... |
| Iodine . . . . | I | 127 | 126.54 | *Thorium* . . . | Th | 232 | ... |
| Iridium . . . . | Ir | 192·5 | ... | Tin (*Stannum*) . | Sn | 118 | 117.35 |
| Iron (*Ferrum*). . | Fe | 56 | 55.88 | *Titanium* . . . | Ti | 48 | ... |
| *Lanthanum* . . | La | 138·5 | ... | *Tungsten* . . . | W | 184 | ... |
| Lead (*Plumbum*). | Pb | 207 | 206.39 | *Uranium* . . . | U | 239·8 | ... |
| Lithium. . . . | Li | 7 | 7.01 | *Vanadium* . . . | V | 51·1 | ... |
| Magnesium . . | Mg | 24 | 23.94 | *Ytterbium* . . . | Yb | 173 | ... |
| Manganese . . | Mn | 55 | 54.8 | *Yttrium* . . . | Y | 89·6 | ... |
| Mercury (*Hydrargyrum* . . | Hg | 200 | 199.8 | Zinc . . . . . | Zn | 65 | 64.88 |
|  |  |  |  | *Zirconium* . . . | Zr | 90·4 | ... |

represented by the symbol $O_3$, while the tetr-atomic character of the phosphorus molecule is expressed in the symbol $P_4$. The composition of compound molecules is expressed by placing the symbols of the atoms which compose such molecules in juxtaposition : thus a molecule consisting of one atom of sodium (symbol

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* Where no values are given in this column, those in the third column may be regarded as accurate.

Na) and one atom of chlorine (symbol Cl) is represented by the united symbols of these two elements, NaCl; a compound consisting of one atom of carbon and one atom of oxygen by the symbols of these two atoms, CO. Such arrangements of symbols representing molecules are termed *molecular formulæ*, or, simply, *formulæ*.

When the molecule contains more than one atom of any particular element, this fact is indicated by the use of numerals placed immediately after the symbol to be multiplied: thus, a molecule of water consists of two atoms of hydrogen and one atom of oxygen, the *formula* for water is therefore $H_2O$. One molecule of ammonia, consisting of an atom of nitrogen with three atoms of hydrogen, is represented by the formula $NH_3$; and a molecule of sulphuric acid, which is an aggregation of two atoms of hydrogen, one atom of sulphur, and four atoms of oxygen, has the formula $H_2SO_4$.

It is sometimes necessary to represent the presence in a molecule of certain groups of atoms, groups which seem to hold together, and often to function as a single atom. This is accomplished by the use of brackets: thus $(NH_4)_2SO_4$ is the formula for a molecule containing one atom of sulphur, four atoms of oxygen, eight atoms of hydrogen, and two atoms of nitrogen; the nitrogen and hydrogen atoms being present as two groups, in each of which one nitrogen atom is associated with four hydrogen atoms. Such groups of atoms are termed *compound radicals*.

When it is required to indicate more than one molecule of the same substance, numerals are placed immediately in front of the formula: thus $2H_2O$ signifies two molecules of water, and $3NH_3$ expresses three molecules of ammonia.

By means of these symbols and formulæ, chemists are enabled to represent, in a concise manner, the various chemical changes which it is the province of chemistry to examine. Such changes are usually termed *chemical reactions*, and they are represented in the form of equations in which the symbols and formulæ of the reacting substances as they are before the change are placed on the left, and those of the substances which result from the change upon the right, thus—

$$H_2 + Cl_2 = 2HCl$$
$$HgCl_2 + 2KI = HgI_2 + 2KCl.$$

The sign + has a different significance as used on the left side of the equation to that which it bears upon the right. On the left hand it implies that chemical action takes place between the substances, while on the opposite side it has the simple algebraic meaning. Thus, the second of the above equations is understood to mean, that when the compounds, mercuric chloride and potassium iodide, are brought together in such a way that chemical action results, a redistribution of the atoms will take place, resulting in the formation of mercury iodide and also potassium chloride.

As further illustrations of the use of chemical symbols, the following three examples may be given as exemplifying the three modes of chemical action mentioned on page 13:—

$$(1)\ NH_3 + HCl = NH_4Cl.$$

Ammonia combines with hydrochloric acid, and gives ammonium chloride.

$$(2)\ H_2SO_4 + Na_2CO_3 = Na_2SO_4 + CO_2 + H_2O.$$

Sulphuric acid combines with normal sodium carbonate, and gives normal sodium sulphate, carbon dioxide, and water.

$$(3)\ (CN)O(NH_4) = (NH_2)_2CO.$$

Ammonium cyanate is converted into urea.

In all cases where the nature of the chemical change is understood, it is capable of expression by such equations, and as matter is indestructible, every atom present in the interacting molecules upon the left of the expression, reappears on the right hand side in some fresh association of atoms.*

* See also Chemical Notation, chapter vii.

# CHAPTER V

## *THE ATOMIC THEORY*

THE atomic view as to the constitution of matter, briefly sketched out in Chapter I., forms a part of what is to-day known as the *atomic theory.*

When chemical changes were carefully studied from a *quantitative* standpoint, four laws were discovered in obedience to which chemical action takes place. These laws are distinguished as the laws of chemical combination. Three of these generalisations refer to quantitative relations as respects *weight;* while one expresses quantitative relations with regard to *volume*, and only relates to matter in the gaseous state.

**I. Law of Constant Proportion.**—*The same compound always contains the same elements combined together in the same proportion by weight;* or expressed in other words, *The weights of the constituent elements of every compound bear an unalterable ratio to each other, and to the weight of the compound formed.*

**II. Law of Multiple Proportions.**—*When the same two elements combine together to form more than one compound, the different weights of one of the elements which unite with a constant weight of the other, bear a simple ratio to one another;* or this law may be stated thus: *When one element unites with another in two or more different proportions by weight, these proportions are simple multiples of a common factor.*

**III. Law of Reciprocal Proportions,** or **Law of Equivalent Proportions.**—*The weights of different elements which combine separately with one and the same weight of another element, are either the same as, or are simple multiples of, the weights of these different elements which combine with each other;* or in other words, *The relative proportions by weight in which the elements, A, B, C, D, &c., combine with a constant weight of another element, X, are the same for their combinations with any other element, Y.*

**IV. Law of Gaseous Volumes,** or **The Law of Gay-Lussac.** —*When chemical action takes place between gases, either elements or compounds, the volume of the gaseous product bears a simple relation to the volumes of the reacting gases.*

These four laws are the foundations upon which the whole superstructure of modern chemistry rests.

(1.) **The Law of Constant Proportions.**—When two substances are mingled together, and remain as a mere mechanical mixture, they may obviously be present in any proportion, and it was at one time thought that when two substances entered into chemical combination with each another, they could do so also in any proportion, and that the composition of the resulting compound would vary from this cause. This belief was finally disproved, and the law of constant proportions definitely established by Proust in the year 1806. The same compound, therefore, however made, and from whatever source obtained, is always found to contain the same elements united together in the same proportion by weight. Thus, common salt, or, to adopt its systematic name, sodium chloride, which is a compound of the two elements sodium and chlorine, may be made by bringing the metal sodium into contact with chlorine gas, when the two elements unite and form this compound. It can also be made by the action of hydrochloric acid upon the metal sodium, or by adding hydrochloric acid to sodium carbonate, and by a variety of other chemical reactions. When the sodium chloride obtained by any or all of these processes is analysed, it is invariably found to contain the elements chlorine and sodium in the proportion by weight of 1 : 0.6479, or, expressed centesimally—

| | |
|---|---|
| Sodium . . | 39.32 |
| Chlorine . . | 60.68 |
| | 100.00 |

and when this is compared with the sodium chloride as found in nature, obtained either from the salt-mines of Cheshire, or the celebrated mines in Galicia, or by evaporating sea-water, it is found that the composition of the compound in all cases is exactly the same. In the same way the compound water, consisting of the two elements hydrogen and oxygen, whether it be prepared synthetically by causing the two elements to unite directly, or obtained from any natural source, as rain, or spring, or river, is found to contain its constituent elements hydrogen and oxygen in the ratio by weight of 1 : 8, or,

| | |
|---|---|
| Hydrogen . . | 11.12 |
| Oxygen . . | 88.88 |
| | 100.00 |

If in the formation of sodium chloride by the direct combination of its constituent elements, an excess of either one or other be present beyond the proportions 39.32 per cent. of sodium and 60.68 per cent. of chlorine, that excess will simply remain unacted upon. If eight parts by weight of hydrogen and eight parts by weight of oxygen be brought together under conditions that will cause chemical action, the eight parts of oxygen will unite with one part of hydrogen, and the other seven parts of hydrogen merely remain unchanged. This fact, that elements are only capable of uniting with each other in certain definite proportions, marks one of the most characteristic differences between chemical affinity and those other forces, such as gravitation, that are usually distinguished as physical forces, for although there are many instances known in which the *extent* to which a chemical action may proceed (that is, the particular proportion of the reacting bodies which will undergo the permutation that results in the formation of different molecules) is influenced by the *mass* of the acting substances, it never governs the proportion in which the elements combine in these compounds.

It follows from the law of constant composition that the sum of the weights of the products of a chemical action will be equal to that of the interacting bodies; and upon the validity of this law depend all processes of quantitative analyses.

(2.) **The Law of Multiple Proportions** was first recognised by Dalton, who investigated certain cases where the same two elements combine together in different proportions, giving rise to as many totally distinct compounds. These proportions, however, were always found to be constant for each compound so produced, so that this law formed no contradiction to the law of constant composition. The simple numerical relation existing between the numbers representing the composition of such compounds will be evident from the following examples. The two[*] compounds of carbon with hydrogen, known as *marsh gas* and *ethylene*, are found to contain these elements in the proportions—

---

[*] In Dalton's day these two substances were the only known compounds of carbon with hydrogen.

| | | | | |
|---|---|---|---|---|
| Marsh gas . . | 1 part by weight of hydrogen with | 3 | parts of | carbon. |
| Ethylene . . | 1 ,, ,, ,, | 6 | ,, | ,, |

The two compounds of carbon with oxygen contain these elements in the proportion—

| | | | | | |
|---|---|---|---|---|---|
| Carbon monoxide . | 1 part of carbon with | 1.334 | parts | of oxygen | by weight. |
| Carbon dioxide . | 1 ,, ,, | 2.667 | ,, | ,, | ,, |

The elements nitrogen and oxygen form as many as five different compounds, in which the two elements are present in the proportions—

| | | | | | |
|---|---|---|---|---|---|
| Nitrous oxide . . | 1 part of nitrogen with | 0.571 | parts | of oxygen | by weight. |
| Nitric oxide . . . | 1 ,, ,, | 1.143 | ,, | ,, | ,, |
| Nitrogen trioxide . | 1 ,, ,, | 1.714 | ,, | ,, | ,, |
| Nitrogen peroxide | 1 ,, ,, | 2.286 | ,, | ,, | ,, |
| Nitrogen pentoxide | 1 ,, ,, | 2.857 | ,, | ,, | ,, |

The relative proportions of carbon combining with a constant weight of hydrogen in the two first compounds are as 1 : 2.

Those of oxygen uniting with a constant weight of carbon in the second example are also as 1 : 2, while in the nitrogen series the relative proportions of oxygen in combination with a constant weight of nitrogen are as 1 : 2 : 3 : 4 : 5.

(3.) **Law of Reciprocal Proportions.**—Known also as the law of proportionality, or the law of equivalent proportions. When the weights of various elements, which were capable of uniting separately with a given mass of another element, were compared together, it was seen that these weights bore a simple relation to the proportions in which these elements combined amongst themselves. For example, the elements chlorine and hydrogen each separately combine with the same weight of phosphorus, the proportions being—

Phosphorus : chlorine = 1 : 3.43
Phosphorus : hydrogen = 1 : 0.097

The elements chlorine and hydrogen can combine together, and they do so in the proportion—

Chlorine : hydrogen = 35.5 : 1
but 35 : 1 = 3.43 : 0.097

Therefore the proportions by weight in which chlorine and hydrogen separately combine with phosphorus, is a measure of the proportion in which they will unite together.

Again, the two elements carbon and sulphur each separately combine with the same weight of oxygen, the proportion being—

Oxygen : carbon = 1 : 0.375
Oxygen : sulphur = 1 : 1

But the elements carbon and sulphur themselves unite together, and in the proportion—

Carbon : sulphur = 0.1875 : 1
but 0.1875 : 1 = 0.375 : 2

Therefore the proportion by weight in which carbon and sulphur separately unite with the same mass of oxygen, is a *simple multiple* of that in which these two elements combine together. These remarkable numerical relations will be rendered still more evident, by comparing the proportions in which the members of a series of elements combine with a constant weight of various other elements: thus—

| Hydrogen. | Sodium. | Potassium. | Silver. | Mercury. | Chlorine. |
|---|---|---|---|---|---|
| 0.02817 | 0.6479 | 1.02 | 3.04 | 2.816 | unite separately with 1 part. |

It will be seen that the proportion in which these numbers stand to each other is as—

1 : 23 : 39 : 107 : 100 : 35.5

Let us now compare these proportions with those in which the same elements unite with a constant weight of the element bromine—

| Hydrogen. | Sodium. | Potassium. | Silver. | Mercury. | Bromine. |
|---|---|---|---|---|---|
| 0.0125 | 0.2875 | 0.4875 | 1.34 | 1.25 | unite with 1 part. |

or as—

1 : 23 : 39 : 107 : 100 : 80

Each of these five elements in like manner combines with oxygen, and the weights which are found to unite with a constant mass of oxygen are—

| Hydrogen. | Sodium. | Potassium. | Silver. | Mercury. | Oxygen. |
|---|---|---|---|---|---|
| 0.125 | 2.875 | 4.875 | 13.38 | 12.5 | unite with 1 part. |

again as—

1 : 23 : 39 : 107 : 100 : 8

ıe same relation will appear in the case of the combination of : five elements with a constant weight of sulphur—

| Hydrogen. | Sodium. | Potassium. | Silver. | Mercury. | Sulphur. |
|---|---|---|---|---|---|
| 0.0625 | 1.4375 | 2.4375 | 6.69 | 6.25 | unite with 1 part. |
| — | | | | | |
| 1 : | 23 : | 39 : | 107 : | 100 | 16 |

is thus evident that the proportions in which the members of a series combine with a constant weight of one element, is the : as that in which they unite with a constant mass of another ent. One part by weight of hydrogen combines with 35.5 ; of chlorine, 80 parts of bromine, 8 parts of oxygen, and 16 ; of sulphur—that is to say, these proportions of these four ents satisfy the chemical affinity of 1 part of hydrogen; they herefore said to be *equivalent.* Twenty-three parts of sodium ewise equivalent to 35.5 parts of chlorine, 80 parts of bromine, ırts of oxygen, and 16 parts of sulphur, and by the same ɔning it is also equivalent to 1 part of hydrogen, 39 parts of ssium, 107 parts of silver, and 100 parts of mercury. These bers, therefore, are known as the *equivalent weights* of the ıents, or their *combining proportions*, and the combining weight ı element may therefore be defined as the smallest weight of element which will combine with 1 part by weight of hydrogen. ɪis law of proportionality, or reciprocal proportion, was disred by Richter, but it was left for Dalton to trace the connecbetween these three generalisations. Dalton adopted and ɔted an ancient theory concerning the ultimate constitution of ter which was expounded by certain of the early Greek philoıers. The exponents of this theory held that matter is built up ıst numbers of minute indivisible particles, in opposition to the gonistic theory believed by others, namely, that matter was ɔlutely homogeneous and capable of infinite subdivision.

alton embraced the ancient doctrine of atoms, and extended it the scientific theory which is to-day known as Dalton's atomic ry, and is accepted as a fundamental creed by modern chemists. ccording to this theory, matter consists of aggregations of ɪte particles, or atoms, which are indivisible. Dalton coned that chemical combination takes place between atoms— is to say, when chemical action takes place between two ıents, it is due to the union of their atoms; the atoms coming juxtaposition with each other under the influence of chemical affinity, are held together by the operation of this force. He further assumed that the atoms of the various elements possessed different relative weights, and that the relations existing between these weights, was the same as that between the weights in which experiment had shown the elements to be capable of combining together. In other words, he said that the numbers representing the *combining proportion* of the elements expressed also the relative weights of the atoms.

Let us now see how this theory satisfies and explains the first three laws of chemical combination.

(1.) **The Law of Constant Composition.**—It has already been shown, p. 25, that the compound sodium chloride, wheresoever and howsoever obtained, contains the elements chlorine and sodium in the proportion—

Chlorine : sodium = 1 : 06479.

These numbers have been shown on p. 28 to represent the combining proportions—

Chlorine : sodium = 35.5 : 23.

Now the atomic theory states, that sodium chloride is formed by the union of *atoms* of chlorine with *atoms* of sodium, and that the relative weights of these atoms is expressed by the combining weights of the elements, namely, 35.5 and 23. If, therefore, sodium is to combine with chlorine, since atoms are indivisible masses, it follows that the compound produced by the union of one atom of each of these two elements must always have the same composition.

(2.) **The Law of Multiple Proportions.**—The ratio in which oxygen combines with hydrogen to form the compound water, is seen on p. 27 to be as 8 : 1. This number 8, therefore, we will for the present argument regard as the relative weight of the atom of oxygen.*

Oxygen combines with carbon as already mentioned, forming two different compounds; in the first, the elements are present in the proportion—

Carbon : oxygen = 1 : 1.334 = 6 : 8

That is to say, in the proportion of one atom of carbon to one atom of oxygen. According to the theory, if the atom of carbon unites with more oxygen than *one* atom, it must at least be with *two* atoms. It may be with three or with four, but as the compound must be formed by the accretion of these indivisible atoms, the increment of oxygen must take place by multiples of 8. When the second compound is examined it is found to contain its constituent elements in the proportion—

---

* For reasons which will be explained later, chemists now regard the number 16 as representing (in round numbers) the relative weight of the atom of oxygen.

$$\text{Carbon : oxygen} = 1 : 2.667 = 6 : 16$$

That is to say, in the proportion of one atom of carbon to two atoms of oxygen. This information respecting the composition of these two compounds is conveyed both in their names and their formulæ. The first is termed carbon *mon*oxide, and its formula is expressed by the symbol $CO$; while the second is distinguished as carbon *di*oxide, and has the symbol $CO_2$.

The difference in the composition of the five compounds that nitrogen forms by union with oxygen, will be made evident by the aid of this theory. The proportion of nitrogen to oxygen in these compounds is—

(1.) Nitrogen : oxygen = 1 : 0.571 = 14 : 8
(2.) Nitrogen : oxygen = 1 : 1.143 = 14 : 16
(3.) Nitrogen : oxygen = 1 : 1.714 = 14 : 24
(4.) Nitrogen : oxygen = 1 : 2.268 = 14 : 32
(5.) Nitrogen : oxygen = 1 : 2.857 = 14 : 40

And it will be seen that the increase in the proportion of oxygen in the compounds, takes place by the regular addition of a weight of that element equal to 8, which at the present stage of the argument we are regarding as representing the relative weight of the atom of oxygen.

(3.) **The Law of Reciprocal Proportions.**—If the illustrations given on p. 27 of the operation of this law be examined in the light of the atomic theory, their explanation will be evident: thus, the relative proportions in which hydrogen and chlorine separately combine with phosphorus is 0.097 : 3.43, and the ratio between these numbers is as 1 : 35.5, which is the proportion in which these two elements are known to unite together to form hydrochloric acid. These numbers, however, represent the relative weights of the *atoms* of these elements, therefore hydrochloric acid may be supposed to be formed by the union of one atom of hydrogen with one atom of chlorine.

Again, the relative weights of carbon and sulphur which separately combine with a constant weight of oxygen, are—carbon 0.375, sulphur 1, and the ratio between these numbers is as 6 : 16.

Carbon and sulphur, however, unite together in the relative proportion—

Carbon : sulphur = 0.1875 : 1 = 6 : 32

Therefore the compound they produce, may be supposed to consist of one atom of carbon, having the relative weight 6, and *two* atoms of sulphur, each with the relative weight 16.

# CHAPTER VI

## *ATOMIC WEIGHTS*

In the third column of the table on page 21, the numbers are given, which are at the present time generally accepted by chemists as representing the approximate atomic weights of the elements. These numbers depart, in many instances, from those arrived at by Dalton's methods; thus, the relative weights of carbon, oxygen, nitrogen, and sulphur, which were found to be equivalent to one part of hydrogen, are carbon = 6,* oxygen = 8, nitrogen = 4.66, sulphur = 16; while the figures given as the approximate atomic weights of these elements in the table, are carbon = 12, oxygen = 16, nitrogen = 14, sulphur = 32. We must now discuss some of the chief reasons for these departures. In the two compounds of carbon and hydrogen known to Dalton, namely, marsh gas and ethylene, the proportions of carbon to hydrogen are—

In ethylene . . . Carbon : hydrogen = 6 : 1.
In marsh gas . . Carbon : hydrogen = 6 : 2.

Dalton therefore concluded that ethylene was a compound containing 1 atom of carbon, united with 1 atom of hydrogen, and to which, therefore, he gave the formula $CH$; and that marsh gas consisted of 1 atom of carbon combined with 2 atoms of hydrogen, and which he accordingly represented by the formula $CH_2$.

There was, however, nothing to prove that the weight of *carbon* was constant in the two compounds, for it will be obvious that the same ratio between the weight of carbon and hydrogen will still be maintained by assuming that the *hydrogen* is constant, and that the carbon varies, thus—

In marsh gas . . Hydrogen : carbon : : 1 : 3.
In ethylene . . Hydrogen : carbon : : 1 : 3 × 2.

---

* These are the numbers which Dalton ought to have obtained had his methods of determination been more exact. The figures he actually found for the combining weights of these four elements were respectively 5, 7, 5, 13.

That is to say, the ratios are not disturbed by the assumption that in marsh gas we have 1 atom of hydrogen combined with 1 atom of carbon, having the relative combining weight of 3, and in ethylene 1 atom of hydrogen united with 2 atoms of carbon.

It will be evident, however, that if we could gain any exact information as to the actual number of atoms which are present in these various molecules, this difficulty would no longer exist.

For example, suppose it were possible to ascertain that in the molecule of marsh gas there were 4 atoms of hydrogen, then as the relative weights of hydrogen and carbon in this compound are as 1 : 3, the weight of the carbon atom would obviously have to be raised from 3 to 12; and if it could be determined that in the ethylene molecule there were also 4 atoms of hydrogen, then seeing that the ratio of hydrogen to carbon in this substance is as 1 : 6, we should conclude that it contained 2 atoms of carbon, of the relative weight not less than 12, and the composition of the two compounds would be expressed by the formulæ, marsh gas $CH_4$, ethylene $C_2H_4$.

Again, the relative weights of hydrogen and oxygen in water are as 1 : 8. If the molecule of water contains only 1 atom of hydrogen, then we conclude that 8 represents the relative weight of the oxygen atom, and the formula for water will be HO. But suppose it to be discovered that there are 2 atoms of hydrogen in a molecule of this compound, then it becomes necessary, in order to retain the ratio between the weight of these constituents (a ratio ascertained by analyses), to double the number assigned to the oxygen atom, and to regard its weight as 16, as compared with 1 atom of hydrogen, and the formula for water in this case would be $H_2O$.

The compound ammonia contains the elements hydrogen and nitrogen in the ratio—

Hydrogen : nitrogen : : 1 : 4.66.

If the molecule of ammonia contains only 1 atom of hydrogen, then 4.66 represents the relative weight of the nitrogen atom, and the formula will be NH; but if it should be found that there are 3 atoms of hydrogen in this molecule, then again the relative weight assigned to the nitrogen must be trebled in order to preserve the ratio, and it will have to be raised from 4.66 to 14 (in round numbers), and the formula for ammonia will be $NH_3$.

From these considerations it will be evident, that it is of the ghest importance to gain accurate knowledge as to the actual mber of atoms which are contained in the molecules of matter—other words, to learn the true atomic composition or structure molecules ; and it may be said that this problem has occupied e minds of chemists from the time that Dalton published his omic weights, in the year 1808, down to the present time. There no single method of general application, by means of which emists are able to determine the atomic weight of an element, t they are guided by a number of independent considerations, me of which are chemical in their character, while others are of physical nature ; and that particular number which is in accord th the most of these considerations, or with what are judged to the most important of them, is accepted as the true atomic ight.

The chief methods employed for determining atomic weights ay be arranged under the following four heads :—

1. Purely chemical methods.
2. Methods based upon volumetric relations.
3. Method based upon the specific heats of the elements.
4. Method based upon the isomorphism of compounds.

As an illustration of the chemical processes from which nic weights may be deduced, the following examples may be n, namely, the case of the two elements oxygen and carbon. ygen combines, as already stated, with hydrogen in the rtion—

$$\text{Hydrogen : oxygen} = 1 : 8.$$

en water is acted upon by the element sodium, the compound omposed and hydrogen is evolved ; and it is found that if mmes of water are so acted on, 1 gramme of hydrogen is d, and 40 grammes of a compound are formed, which s sodium, together with all the oxygen originally in the mes of water, and some hydrogen. This compound, under conditions, can be again acted upon by sodium, and when grammes are so acted on, 1 gramme of hydrogen is again and 62 grammes are obtained of a compound containing gen, but sodium combined with all the oxygen originally d in the 18 grammes of water.

be evident, therefore, that the hydrogen contained in be expelled in two equal moieties ; there must, therefore, oms of *hydrogen in this compound.* By no known process can the *oxygen* be withdrawn from water in two stages; thus, if 18 grammes of water are acted upon by chlorine, under the conditions in which chemical action can take place, 71 grammes of a compound containing only chlorine and hydrogen are found, and the whole of the oxygen is thrown out of combination, and evolved as gas. It is therefore concluded, that water contains in its molecule, 2 atoms of hydrogen and 1 atom of oxygen, and as they are combined in the relative proportion of 1 : 8, the atomic weight of oxygen cannot be less than 16.

No compounds have been found in which a smaller weight of oxygen, relative to one atom of hydrogen, than is represented by the number 16 (approximately), is known to take part in a chemical change.

The compound *marsh gas* contains hydrogen and carbon in the proportion by weight of 1 : 3. By acting on this compound with chlorine, it is possible to remove the hydrogen from it in four separate portions.

By the first action of chlorine upon 16 grammes of marsh gas, 1 gramme of hydrogen is removed in combination with 35.5 grammes of chlorine, and a compound containing carbon, hydrogen, and chlorine, in the ratio 12 : 3 : 35.5, is formed.

By the successive action of chlorine, three other moieties of hydrogen can be thus withdrawn, each being in combination with its equivalent (35.5 parts) of chlorine. The second and third compounds that are formed contain carbon, hydrogen, and chlorine in the ratios $12 : 2 : (35.5 \times 2)$ and $12 : 1 : (35.5 \times 3)$.

The compound produced by the fourth action of chlorine, which withdraws the fourth portion of hydrogen, contains only carbon and chlorine, in the ratio $12 : (35.5 \times 4)$. From the fact that the hydrogen contained in marsh gas can thus be removed in four separate portions, the molecule must contain four hydrogen atoms, and therefore the atomic weight of carbon must be at least 12. No compounds of carbon are known in which a smaller weight of carbon, relative to one atom of hydrogen, than is represented by the number 12, takes part in a chemical change.

The definition of atomic weight, furnished by considerations of a chemical nature, may be thus stated: the atomic weight of an element, is the number which represents how many times heavier the smallest mass of that element capable of taking part in a chemical change is, than the smallest weight of hydrogen which can so function.

The choice of hydrogen as the unit of atomic weights is a purely arbitrary lection ; but since atomic weight values can only be determined *relatively*, it ecomes necessary to select some one element and to assign to its atom some articular number to serve as a standard. As hydrogen is the lightest of all ements, Dalton originally adopted it, and arbitrarily fixed unity as the umber which should stand for its atomic weight. The disadvantages of this articular unit are twofold: in the first place the number of elements that form ydrogen compounds that are suitable for atomic weight determinations is very nall, whereas nearly all the elements form convenient oxygen compounds, or mpounds with elements whose atomic weights with reference to oxygen are ccurately known, and in actual practice such compounds are almost always ade use of for such determinations. In the second place, the *exact* ratio of e weights of an atom of hydrogen and oxygen is not known with certainty, so at in calculating atomic weights that are determined with reference to oxygen, ossible errors may arise. The ratio Hydrogen : Oxygen is *not* exactly 1 : 16. arious values have been obtained by different experimenters, and at the present me 1 : 15.96 is accepted as more nearly the truth.

On account of the extreme difficulty of exactly determining this ratio, hemists are now generally agreed in adopting as the unit in all exact determiations of atomic weights, a number which is $\frac{1}{16}$th the weight of the atom of xygen: that is to say, the atomic weight of oxygen is in reality the standard, nd is fixed as 16, and the unit, instead of being the weight of 1 atom of ydrogen, is $\frac{1}{16}$th of this number.

The effect of this change is only of importance in cases of chemical investigaion where a high degree of exactitude is required ; for purposes of ordinary nalyses and chemical calculations the difference that it makes is practically *nil*. ixing the atomic weight of oxygen at 16 merely raises the atomic weight of ydrogen from 1 to 1.003. As the use of small decimal fractions introduces nnecessary complications which tend to obscure simple processes of reasoning, he approximate atomic weights given in the third column of page 21, will be mployed for the most part in the following Introductory chapters.

2. **Determination of Atomic Weights from Considerations ased upon Volumetric Relations. The Law of Gaseous olumes.**—In the year 1805 the fact was discovered by Gay ussac and Humboldt, that when 1 litre of oxygen combines with litres of hydrogen, the vapour of water (or steam) which was roduced, occupied 2 litres, the volumes in all cases being measured nder the same conditions of temperature and pressure.* This act led to the discovery of the simple relation existing between he volumes of other reacting gases and the volume of the products : hus it was found that—

1 vol. of hydrogen unites with 1 vol. of chlorine, and gives 2 vols. of hydrochloric acid.

---

* For the relations of gaseous volumes to temperature and pressure the student is referred to chapter ix., on the *general properties* of gases.

1 vol. of hydrogen unites with 1 vol. of bromine vapour, and gives 2 vols. of hydrobromic acid.

2 vols. of hydrogen unite with 1 vol. of oxygen, and give 2 vols. of steam.

2 vols. of carbon monoxide unite with 1 vol. of oxygen, and give 2 vols. of carbon dioxide.

1 vol. of carbon monoxide unites with 1 vol. of chlorine, and gives 1 vol. of phosgene gas.

In the same way with compounds that cannot be obtained by the direct union of their constituent elements, it is found that on being subjected to processes of decomposition, similar simple volumetric relations exist: thus by suitable methods of decomposition—

2 vols. of ammonia gas yield 1 vol. of nitrogen and 3 vols. of hydrogen.

2 vols. of nitrous oxide yield 2 vols. of nitrogen and 1 vol. of oxygen.

2 vols. of nitric oxide yield 1 vol. of nitrogen and 1 vol. of oxygen.

1 vol. of marsh gas yields 2 vols. of hydrogen and some solid carbon, which cannot be evaporated, and therefore its vapour volume is unknown.

1 vol. of ethylene yields 2 vols. of hydrogen and solid carbon as in the preceding.

The observations of these and similar facts gave rise to the law of Gay Lussac, and it will be seen that there is evidently a close connection between the simple *volumetric* relations, and those existing between the multiple proportions by *weight*, in which one element unites with another. For example, in the two oxides of nitrogen the ratios of the two elements by weight are—

Nitrous oxide . . Nitrogen : oxygen = 28 : 16.
Nitric oxide . . . Nitrogen : oxygen = 28 : (16 × 2),

while the volumetric relation in which the two constituents are present is—

Nitrous oxide . . Nitrogen : oxygen = 2 : 1.
Nitric oxide . . . Nitrogen : oxygen = 2 : (1 × 2).

In other words, there is twice as much oxygen by *weight* in the one compound as in the other, and there is twice as much oxygen by *volume* in the one as compared to the other. Moreover, if 14 and 16 respectively represent the relative weights of atoms of nitrogen and oxygen, then the numbers representing the relative *volumes* in which these elements unite will also express the number of atoms of each in the molecule.

The connection existing between the proportions in which elements unite by weight, and by volume, was first explained by the Italian physicist and chemist Avogadro, who in the year 1811 advanced the theory now recognised as a fundamental principle, and known as Avogadro's hypothesis. This theory may be thus stated: *Equal volumes of all gases or vapours, under the same conditions of temperature and pressure, contain an equal number of molecules.* If this be true, if there are the same *number* of molecules in equal volumes of all gases, it must follow that the ratio between the weights of equal volumes of any two gases, will be the same as that between the single molecules of the particular gases. If a litre of oxygen be found to weigh sixteen times as much as a litre of hydrogen (under like conditions of temperature and pressure), inasmuch as there are the same number of molecules in each, the oxygen molecule must be sixteen times heavier than that of hydrogen; and therefore, by the comparatively simple method of weighing equal volumes of different gases, it becomes possible to arrive at the relative weights of their molecules.

The relative weights of equal volumes of gases and vapours, in terms of a given unit, are known as their *densities* or *specific gravities.* Sometimes densities are referred to air as the unit, but more often hydrogen, as being the lightest gas, is taken as the standard. Taking hydrogen as the unit, the density or specific gravity of a gas, is the weight of a given volume of it, as compared with the weight of the same volume of hydrogen—or in other words, the ratio between the weight of a molecule of that gas, and a molecule of hydrogen. The ratio that exists between the weight of a gaseous molecule and *half the weight of a molecule of hydrogen*, chemists term the *molecular weight* of that gas; hence it will be obvious that the number which represents the molecular weight of a gas, is double that of its density or specific gravity.

If 1 litre of hydrogen and 1 litre of chlorine be caused to combine, 2 litres of gaseous hydrochloric acid are formed. As equal volumes of all gases (under like conditions) contain the same number of molecules, in the 2 litres of hydrochloric acid there must be twice as many molecules of that compound, as there were of hydrogen molecules in the 1 litre, or of chlorine molecules in the other. But each molecule of hydrochloric acid is composed of chlorine and hydrogen (from other considerations one atom of each element), therefore there must have been at least twice as many atoms of hydrogen, in the litre of that gas, as there were molecules; and by the same reasoning, twice as many chlorine atoms in the litre of chlorine, as there were molecules: in other words, both hydrogen and chlorine molecules consist of *two* atoms. The molecular weight of hydrogen therefore is 2; that is, its molecule is twice as heavy as its atom. The *atom* of hydrogen is the unit to which molecular weights are referred, while the weight of the molecule of hydrogen is taken as the standard of densities or specific gravities.

In order, therefore, to find the molecular weight of any gas or vapour, it is necessary to learn its density—that is, to ascertain how many times a given volume of it is heavier than the same volume of hydrogen,* and to double the number so obtained.†

The following table gives the densities or specific gravities of all the elements whose vapour densities have been determined. The list includes all those elements which are gases at the ordinary temperature, and those that can be vaporised under conditions which render such determinations experimentally possible. (Hydrogen being taken as unity, the other numbers are the approximate values, which for purposes of discussion are more suitable than figures that run to two or three decimal places.)

| | | | |
|---|---|---|---|
| Hydrogen | 1 | Iodine | 127 |
| Nitrogen | 14 | Sodium | 11.5 |
| Oxygen | 16 | Potassium | 19.5 |
| Fluorine | 19 | Zinc | 32.5 |
| Sulphur | 32 | Cadmium | 56 |
| Chlorine | 35.5 | Mercury | 100 |
| Selenium | 79 | Phosphorus | 62 |
| Bromine | 80 | Arsenic | 150 |

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* Certain exceptions to this rule are discussed under the subject of Dissociation, chap. x., p. 85.

† The specific gravity of hydrogen, as compared with air taken as unity, is 0.0693, or air is 14.43 times heavier than hydrogen. If, therefore, it be desired to find the molecular weight of a given gas, whose density as compared with air is known, it is only necessary to multiply its density (air = 1) by the number 14.43, which gives its density as compared with hydrogen, and then to double the number so obtained.

Let us now consider how the knowledge of the relative weights of gaseous molecules is utilised, in assigning a particular number as the atomic weight of an element.

The molecular weight of chlorine is 71. It has been shown that the molecule certainly contains more than 1 atom, and *probably* 2, in which case 35.5 would represent the relative weight of the atom.

The compound hydrochloric acid has the molecular weight 36.5. It has been already proved that this compound contains 1 atom of hydrogen, therefore $36.5 - 1 = 35.5$.

The compound carbon tetrachloride gives a molecular weight 154. Analysis shows that this compound contains 12 parts of carbon in 154 parts, therefore $154 - 12 = 142 = 35.5 \times 4$.

In these three molecules the weights of chlorine relative to the weight of 1 atom of hydrogen are 142, 35.5, and 71, the greatest common divisor of which is 35.5. This number, therefore, is selected as the atomic weight of chlorine.

Again, it has been shown that by the action of sodium upon water, the hydrogen contained in the water could be expelled in two separate portions, thus proving that there must be 2 atoms of hydrogen in the molecule of that compound.

The molecular weight of water is found to be 18, deducting from this the weight of the two hydrogen atoms we get $18 - 2 = 16$.

The molecular weight of carbon monoxide is 28; 28 parts of this compound contain 12 parts of carbon, therefore $28 - 12 = 16$.

The molecular weight of carbon dioxide is 44; 44 parts of this compound also contain 12 parts of carbon, therefore $44 - 12 = 32$.

When 1 litre of oxygen combines with two litres of hydrogen, 2 litres of water vapour are formed; there are therefore twice the number of water molecules produced as there are oxygen molecules (since by Avogadro's hypothesis 2 litres contain twice as many molecules as 1 litre). But each water molecule contains certainly 1 atom of oxygen, therefore the original oxygen molecules must have consisted of not less than 2 atoms. When the density of oxygen is determined it is found to be 16, its molecular weight therefore is 32.

In these four various molecules the weights of oxygen relative to the weight of 1 atom of hydrogen are 16, 16, 32, 32, the greatest common divisor of which is 16. This number, therefore, is selected as the atomic weight of oxygen.

Again, it has already been shown that in the compound ammonia, the hydrogen can be removed in three separate moieties, proving that there must be three atoms of that element in the molecule. The molecular weight of ammonia is found to be 17, therefore $17 - 3 = 14$, which is the weight of the nitrogen.

The molecular weight of nitrous oxide is 44; 44 parts of this compound are found to contain 16 parts of oxygen and 28 parts of nitrogen.

The molecular weight of nitric oxide is 30; 30 parts of this compound contain 16 parts of oxygen and 14 parts of nitrogen.

The molecular weight of nitrogen is found to be 28.

In these four different molecules the weights of nitrogen relative to the weight of 1 atom of hydrogen are 14, 28, 14, 28, the greatest common divisor of which is 14. The atomic weight of nitrogen, therefore, is regarded as 14.

These three examples, namely, chlorine, oxygen, and nitrogen are instances of elements which are gaseous at ordinary temperatures; but the same methods are applicable in the case of the non-volatile elements, such as carbon, provided they furnish a number of compounds that are readily volatile.

On comparing the numbers in the foregoing table (p. 40), representing the densities of various elements, with the atomic weights of those elements as given on p. 21, it will be seen that in the first nine cases the numbers given are approximately the same. This agreement is merely because the molecules of these elements consist of two atoms. The molecules of sodium, potassium, zinc, cadmium, and mercury consist of only one atom; their atomic weights, therefore, will be the same as their molecular weights, that is, twice their densities. The elements arsenic and phosphorus, on the other hand, contain in their molecules four atoms—that is to say, the number which represents the smallest weight of phosphorus, and of arsenic, capable of taking part in a chemical change, is only half the density, and therefore a fourth of the molecular weight.

The definition of atomic weight that is furnished by the consideration of volumetric relations may be thus stated. *The atomic weight is the smallest weight of an element that is ever found in a volume of any gas or vapour equal to the volume occupied by one molecule of hydrogen, at the same temperature and pressure.*

The volume occupied by one molecule of hydrogen is regarded as the standard molecular volume, while that occupied by an atom of hydrogen—or, in other words, the atomic volume of hydrogen—is called the *unit volume.* The standard molecular volume therefore is said to be *two unit volumes;* and as, from Avogadro's law, all gaseous molecules have the same volume, it follows that the molecules of all gases and vapours occupy two unit volumes. Atomic weight may therefore be defined as ***the smallest weight of an element ever found in two unit volumes of any gas or vapour.***

The molecular volume of a gas is its molecular weight divided by its relative density, a ratio which in all cases will obviously equal 2, that is, two unit volumes.

The atomic volume of an element in the state of vapour, is its atomic weight divided by its relative density. In the case of such elements as chlorine, nitrogen, oxygen, &c., whose molecules are diatomic, the quotient will be 1—that is to say, the atomic volumes of these elements is equal to 1 unit volume. In the case of mercury vapour, however, we have $\frac{\text{atomic weight} = 200}{\text{density} = 100} = 2$.

The atomic volume of mercury vapour, therefore, is equal to 2 unit volumes, and is identical with its molecular volume.

On the other hand, with the element phosphorus the atomic volume is $\frac{\text{atomic weight} = 31}{\text{density} = 62} = .5$, or one-half the unit volume, and therefore one-fourth the molecular volume; consequently, four atoms exist in this molecule.

The method of determining atomic weights based upon volumetric relations, when taken by itself, is not an absolutely certain criterion, for although the atomic weight of an element cannot be *greater* than the smallest mass that enters into the composition of the molecules of any of its known compounds, it might be *less* than this, as there is always the possibility of a new compound being discovered, in which the relative weight of an element is such as to make it necessary to halve the previously accepted atomic weight.

3. **Determination of Atomic Weight from the Specific Heat of Elements in the Solid State.**—When equal weights of different substances are heated through the same range of temperature, it is found that they absorb very different quantities of heat, and on again cooling to the original temperature, they consequently give out different amounts of heat. Thus, if 1 kilogramme of water, and 1 kilogramme of mercury, be each heated to a temperature of 100°, and then each be poured into a separate kilogramme of water at 0°, in the first case the resultant mixture will have a temperature of 50°, while in the second it will only reach the temperature of 3.2°; that is to say, while the water in cooling through 50° has raised the temperature of an equal weight of water from 0° to 50°, the amount

of heat in 1 kilogramme of mercury at 100° has only raised the temperature of an equal weight of water from 0° to 3.2°, and in so doing has itself become lowered in temperature 100 − 3.2 = 96.8°. The amount of heat contained, therefore, in equal weights of water and of mercury at the same temperature, as shown by these figures, is as—

$$\frac{50}{50} : \frac{3.2}{96.8} = 1 : \frac{1}{30} ;$$

therefore it requires 30 times as much heat to raise a given weight of water through a given number of degrees as to raise an equal weight of mercury through the same interval of temperature, or the *thermal capacity* of mercury is $\frac{1}{30}$th that of water.

The specific heat of a substance is the ratio of its thermal capacity to that of an equal weight of water; or, the ratio between the amount of heat necessary to raise a unit weight of the substance from 0° to 1°, and that required to raise the same weight of water from 0° to 1°; thus, the specific heat of mercury is $\frac{1}{30}$, or 0.033. Water is chosen as the standard of comparison because it possesses the highest thermal capacity of all known substances; the numbers, therefore, which express the specific heats of other substances are all less than unity.

Dulong and Petit were the first to draw attention (1819) to a remarkable relation which exists between the specific heats, and the atomic weights, of various solid elements, whose specific heats they themselves had determined. They found that the specific heats of the solid elements were inversely as their atomic weights; that is to say, the capacity for heat of masses of the elements proportional to their atomic weight, was equal. This law, known as the law of Dulong and Petit, may be thus stated: *The thermal capacities of atoms of all elements in the solid state are equal.*

The thermal capacity of an atom is termed its *atomic heat;* hence the law may be more briefly stated, *all elements in the solid state have the same atomic heat.* This important constant, is the product of the atomic weight into the specific heat. From the following table it will be seen that the number expressing the atomic heat is not perfectly constant: the departures from the mean 6.4 are, as a rule, only slight, and may be attributed to the fact that the determinations are not always made upon the elements under conditions that are strictly comparable. At the end of the table, however, there are certain elements which appear to present marked exceptions to the law.

| Element. | Specific Heat. | | Atomic Weight. | | Atomic Heat. |
|---|---|---|---|---|---|
| Lithium | 0.94 | × | 7 | = | 6.6 |
| Sodium | 0.29 | × | 23 | = | 6.7 |
| Potassium | 0.166 | × | 39 | = | 6.5 |
| Manganese | 0.122 | × | 55 | = | 6.7 |
| Iron | 0.112 | × | 56 | = | 6.3 |
| Silver | 0.057 | × | 108 | = | 6.1 |
| Gold | 0.032 | × | 196 | = | 6.2 |
| Mercury (solid) | 0.032 | × | 200 | = | 6.4 |
| Lead | 0.031 | × | 206.4 | = | 6.5 |
| Beryllium | 0.41 | × | 9.1 | = | 3.7 |
| Boron (cryst.) | 0.25 | × | 11 | = | 2.75 |
| Carbon (diamond) | 0.147 | × | 12 | = | 1.76 |
| Silicon (cryst.) | 0.177 | × | 28 | = | 4.95 |

It will be seen that, relatively speaking, the four elements which show a considerable departure from the law of Dulong are elements with low atomic weights. Low atomic weight, however, is not *always* accompanied by such deviation, as is shown in the case of lithium and sodium.

When the different allotropes of carbon are experimented upon, it is found that the departure is not the same for each modification of the element, thus—

| Element. | Specific Heat. | | Atomic Weight. | | Atomic Heat. |
|---|---|---|---|---|---|
| Diamond | 0.147 | × | 12 | = | 1.76 |
| Graphite | 0.200 | × | 12 | = | 2.40 |
| Charcoal | 0.241 | × | 12 | = | 2.90 |

It has been observed that, as a general rule, the specific heat of an element is slightly higher at higher temperatures; but in the case of the four elements showing abnormal atomic heats, this increase rises rapidly with increased temperature, until a certain point is reached, when it remains practically constant, and represents an atomic heat which closely approximates to the normal value; thus in the case of diamond, the specific heat at increasing temperatures is—

| | Specific Heat. | | Atomic Weight. | | Atomic Heat. |
|---|---|---|---|---|---|
| Diamond at 10.7° | 0.1128 | × | 12 | = | 1.35 |
| „ 45° | 0.1470 | × | 12 | = | 1.76 |
| „ 206° | 0.2733 | × | 12 | = | 3.28 |
| „ 607° | 0.4408 | × | 12 | = | 5.30 |
| „ 806° | 0.4489 | × | 12 | = | 5.4 |
| „ 985° | 0.4589 | × | 12 | = | 5.5 |

The same result is seen in the case of graphite, and it is also to be remarked, that while at low temperatures there exists a wide difference between the specific heats of these two modifications of carbon, this difference vanishes at a temperature of about 600°.

| | Specific Heat. | | Atomic Weight. | | Atomic Heat. |
|---|---|---|---|---|---|
| Graphite at 10.8° . . . . | 0.1604 | × | 12 | = | 1.93 |
| " 61.3° . . . . | 0.1990 | × | 12 | = | 2.39 |
| " 642° . . . . | 0.4454 | × | 12 | = | 5.35 |
| " 978° . . . . | 0.4670 | × | 12 | = | 5.50 |

Both the elements boron and silicon are found to follow the same rule, and at moderate temperatures their atomic heats nearly approximate the normal constant.

The case of the somewhat rare element beryllium is of special interest from another point of view, which will be referred to when treating of the natural classification of the elements: from the following numbers * it will be seen that its atomic heat very rapidly rises with moderate increase of temperature.

| | Specific Heat. | | Atomic Weight. | | Atomic Heat. |
|---|---|---|---|---|---|
| Beryllium at 100° . . . . | 0.4702 | × | 9.1 | = | 4.28 |
| " 200° . . . . | 0.5420 | × | 9.1 | = | 4.93 |
| " 400° . . . . | 0.6172 | × | 9.1 | = | 5.61 |
| " 500° . . . . | 0.6206 | × | 9.1 | = | 5.65 |

The relation between atomic weight and specific heat, established by Dulong and Petit, is of service in the determination of atomic weights, not as a method of ascertaining the exact value with any degree of refinement, but rather as a means of deciding between two numbers which are multiples of a common factor.

If specific heat × atomic weight = atomic heat, it will be obvious that, if we experimentally determine the specific heat, and divide that value into the constant atomic heat, 6.4, we obtain the approximate atomic weight.

The two following examples will serve to illustrate the application of the method.

The element indium combines with chlorine in the proportion—

Indium : chlorine = 37.8 : 35.5

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* Humpidge.

If InCl is the formula, then 37.8 is the atomic weight of indium; but from the chemical similarity between indium and zinc (whose chloride has the formula $ZnCl_2$), it was believed that the formula for indium chloride was $InCl_2$, in which case, in order to preserve the ratio between the two elements, the atomic weight would have to be 37.8 × 2 = 75.6.

When the specific heat of indium was determined,* it was found to be 0.057.

$$\frac{6.4}{0.057} = 112.28$$

Therefore the atomic weight must be raised by ~~one-third~~ one half, from 75.6 to 113.4, and the formula for the chloride will be $InCl_3$.

The element thallium combines with chlorine in the proportion—

$$\text{Thallium : chlorine} = 203.6 : 35.5$$

In some of its compounds thallium exhibits a strong resemblance to potassium, the chloride of which has the formula KCl. If the formula for the thallium chloride is TlCl, the atomic weight of the metal must be 203.6.

In many respects thallium exhibits a striking analogy with lead, the chloride of which has the formula $PbCl_2$. If thallium chloride has a corresponding formula, $TlCl_2$, then the atomic weight of thallium must be raised to 407.2.

When the specific heat of thallium was ascertained,† it was found to be 0.0335.

$$\frac{6.4}{0.0335} = 191.3$$

This result shows that the number 203.6 and not 407.2 is the atomic weight of thallium, and that the chloride has the formula TlCl.

**Molecular Heat of Compounds.**—The capacity for heat of an atom, undergoes no alteration when the atom enters into combination with different atoms—in other words, the atomic heat of an element is the same in its compounds. The *molecular heat* of a compound (that is, the product of the molecular weight into the specific heat) will therefore be the sum of the atomic heats of its constituent elements. Hence it is possible to calculate what will be the atomic heat of an element, which does not exist as a solid under ordinary conditions; and therefore the atomic weight of such an element, as deduced from other considerations, is capable of verification, by determinations of the molecular heat of various of its compounds: thus—

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* Bunsen, 1870.

† Regnault.

The specific heat of silver chloride, AgCl, is 0.089:—

| Specific Heat. | | Molecular Weight. | | Molecular Heat. |
|---|---|---|---|---|
| 0.089 | × | 143.5 | = | 12.77. |

The atomic heat of silver = 6.1, therefore, as deduced from this compound, the atomic heat of chlorine is 12.77 − 6.1 = 6.6.

Again, the specific heat of stannous chloride, $SnCl_2$, is 0.1016:—

| Specific Heat. | | Molecular Weight. | | Molecular Heat. |
|---|---|---|---|---|
| 0.1016 | × | 189 | = | 19.2. |

The atomic heat of tin is 6.6, therefore the atomic heat of two atoms of chlorine, as deduced from this compound, is 19.2 − 6.6 = 12.6, giving 6.3 as the atomic heat of chlorine.

The differences that appear in the value, as deduced from various compounds, are lessened, because the errors of the method are more equally distributed, if we divide the molecular heat by the number of atoms in the molecule. Thus, in the two examples quoted, silver chloride consists of two atoms, while the molecule of stannous chloride contains three; if, therefore, the molecular heats of these two compounds are divided respectively by 2 and by 3 we get—

$$\frac{12.77}{2} = 6.38, \text{ and } \frac{19.2}{3} = 6.4,$$

as the value representing the atomic heat of chlorine.

The element calcium combines with chlorine in the proportion—

Calcium : chlorine = 20 : 35.5.

If the atomic weight of calcium is 20, the formula will be *CaCl*, whereas if 40 is the atomic weight of the metal, the compound must be represented by the formula $CaCl_2$.

The molecular weight of *CaCl* would be 55.5, that of $CaCl_2$ 111.0.

When the specific heat of the compound was determined, it was found to be 0.1642. In order, therefore, to decide between the two values for the atomic weight of calcium, we calculate the molecular heat from both of the molecular weights, and divide the result by the number of atoms in the molecule in each case.

On the supposition that Ca = 20, and that *CaCl* represents the chloride :—

$$CaCl \quad . \quad . \quad . \quad \frac{0.1642 \times 55.5}{2} = 4.55.$$

Or, if Ca = 40, and $CaCl_2$ is the formula for the chloride, then—

$$CaCl_2 . \quad . \quad . \quad \frac{0.1642 \times 111.0}{3} = 6.07.$$

The number 6.07, which nearly agrees with the constant 6.4, decides the value 40 as the atomic weight of calcium. The element calcium is one of those metals which it is very difficult to isolate and obtain in a state of purity, but when in recent years the specific heat of this metal was experimentally determined,* it was found to be 0.1704 :—

$$0.1704 \times 40 = 6.8.$$

Thus affording direct confirmation of the value 40 for the atomic weight of calcium, which had been deduced from the molecular heat of its compounds.

Deductions based upon molecular heats of compounds, are only trustworthy in the case of the most simply constituted compounds.

4. **Determination of Atomic Weight from Considerations based on Isomorphism.**—It was early observed that certain relations existed between the crystalline forms of compounds, and their chemical composition. Mitscherlich found that certain substances having an analogous chemical composition, as for example, sodium phosphate and sodium arsenate, crystallised in the same geometric form. In the year 1821 he stated his *law of isomorphism* as follows : "The same number of atoms, combined in the same way, give rise to the same crystalline form, which is independent of the chemical nature of the atoms, being influenced only by their number and mode of arrangement." Subsequent investigations, however, have shown that this statement is too general.

In its broad sense, as signifying the same crystalline form, isomorphism is found to exist—

1. Between compounds containing the same number of atoms

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* Bunsen.

similarly combined, and which bear close chemical analogies to each other.

| | | |
|---|---|---|
| Isomorphous | Zinc sulphate . . . . | $ZnSO_4,7H_2O$. |
| | Magnesium sulphate . . . | $MgSO_4,7H_2O$. |
| Isomorphous | Hydrogen disodium phosphate . | $HNa_2PO_4,12H_2O$. |
| | Hydrogen disodium arsenate . | $HNa_2AsO_4,12H_2O$. |
| Isomorphous | Rubidium alum . . . . | $Rb_2SO_4,Al_2(SO_4)_3,24H_2O$. |
| | Potassium chrome alum . . | $K_2SO_4,Cr_2(SO_4)_3,24H_2O$. |
| | Potassium aluminium selenium lum . . . . | $K_2SeO_4,Al_2(SeO_4)_3,24H_2O$. |

2. Between compounds containing a different number of atoms, but which also bear close chemical analogies to one another.

| | | |
|---|---|---|
| Isomorphous | Ammonium chloride . . . | $NH_4Cl$. |
| | Potassium chloride . . . | $KCl$. |
| Isomorphous | Ammonium sulphate . . . | $(NH_4)_2SO_4$. |
| | Potassium sulphate . . . | $K_2SO_4$. |

3. Between compounds containing either the same or a different number of atoms, and which exhibit little or no chemical analogies.

| | | |
|---|---|---|
| Isomorphous | Sodium nitrate . . . . | $NaNO_3$. |
| | Calcium carbonate . . . | $CaCO_3$. |
| Isomorphous | Sodium sulphate (anhydrous) . | $Na_2SO_4$. |
| | Barium permanganate . . | $BaMn_2O_8$. |

Isomorphism of this order, where little or no chemical relations exist between the compounds, is sometimes distinguished as *isogonism*. It must not be supposed, that because two chemically analogous compounds contain the same number of atoms, they will necessarily crystallise in the same form: there are indeed a large number of similarly constituted analogous compounds that do not exhibit isomorphism.

No simple definition of isomorphism is possible, but the following test is generally accepted as a criterion, namely, the power to form either *mixed crystals* or *layer crystals*. Thus, when two substances are mixed in a state of liquidity, and allowed to crystallise, if the crystals are perfectly homogeneous, they are known as *mixed crystals*, and the substances are regarded as isomorphous.

Or when a crystal of one compound is placed in a solution of another compound, and the crystal continues to grow regularly *in* the liquid, the compounds are isomorphous. Thus, if a crystal of potassium alum (white) be placed in a solution of manganese alum, the crystal continues to grow without change of form, and a layer of amethyst-coloured manganese alum is deposited upon it.

In making use of the law of isomorphism in the determination of atomic weights, it is assumed that the weights of different atoms that can mutually replace each other without altering the crystalline form, are proportional to their atomic weights.*

Thus, if we suppose that, in the case of the sulphates of zinc and magnesium, the atomic weight of zinc is known, viz., 65, and that of magnesium is doubtful; from the fact of the isomorphism of the sulphates it may be premised that the elements are present in proportions relative to their atomic weights. Analysis shows that the proportion is 24 of magnesium to 65 of zinc, therefore 24 is presumably the atomic weight of magnesium.

In this way Berzelius corrected many of the atomic weights which in his day had been assigned to the elements.

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* The group $(NH_4)$ may be regarded as an atom, having the relative weight 18.

# CHAPTER VII

## *QUANTITATIVE CHEMICAL NOTATION*

THE use of chemical symbols and formulæ, as a convenient means of representing concisely the qualitative nature of chemical changes, has been explained in chapter iv. We are now in a position to read into these symbols a quantitative significance, which at that stage it would have been premature to explain.

The symbol of an element stands for an atom; but, as we have now learnt, the atoms of the various elements have different relative weights, hence these symbols represent relative weights of matter. The symbol Na signifies 23 relative parts by weight of sodium, O stands for 16 relative parts by weight of oxygen, H for 1 part of hydrogen; in other words, the weight of sodium represented by the symbol Na, is 23 times as heavy as that which is conveyed by the symbol H. A chemical equation, therefore, is a strictly quantitative expression, in which certain definite weights of matter are present in the form of the reacting substances, and which reappear without loss or gain in the compounds resulting from the change. In this sense a chemical equation is a mathematical expression. Thus, the equation—

$$\mathrm{Na + Cl = NaCl},$$

not only means that an atom of sodium combines with an atom of chlorine and forms 1 molecule of sodium chloride, but it also means

$$\begin{array}{ccccc} 23 & + & 35.5 & = & 58.5 \\ \mathrm{Na} & & \mathrm{Cl} & & \mathrm{NaCl.} \end{array}$$

In other words, that sodium and chlorine unite in the relative proportion of 23 parts of the former, and 35.5 parts of chlorine, and produce 58.5 parts of sodium chloride.

In the same way, into the equation which expresses the action of sulphuric acid upon sodium carbonate, we read the quantitative meaning of the symbols—

$$\begin{array}{ccccccccc} \mathrm{H_2SO_4} & + & \mathrm{Na_2CO_3} & = & \mathrm{Na_2SO_4} & + & \mathrm{CO_2} & + & \mathrm{H_2O}. \\ 2 & & 46 & & 46 & & & & \\ 32 & & 12 & & 32 & & 12 & & 2 \\ 64 & & 48 & & 64 & & 32 & & 16 \\ \hline 98^{*} & + & 106 & = & 142 & + & 44 & + & 18 \end{array}$$

That is to say, 98 parts by weight of sulphuric acid act upon 106 parts of sodium carbonate, producing 142 parts of sodium sulphate, 44 parts of carbon dioxide, and 18 parts of water. It will be evident that it becomes a matter of the simplest arithmetic, to calculate the weight of any product that can be obtained from a given weight of the reacting substances; or *vice versâ*, to find the weight of any reacting substance which would be required to produce a given weight of the product of the action.

Not only is information respecting the quantitative relations by *weight* embodied in a chemical equation, but when gaseous substances are reacting, the equation also represents the volumetric relation between the gases. In order that the volumetric relations may be more manifest, the equations expressing the reactions are written in such a manner as to represent the molecules of the substances.

$$\mathrm{H + Cl = HCl}$$

is an *atomic* equation, but as the molecule is the smallest particle which can exist alone, a more exact statement of the chemical change is made, by representing the action as taking place between molecules, thus—

$$\mathrm{H_2 + Cl_2 = 2HCl.}$$

From such an equation we see that 1 molecule of hydrogen, or 2 unit volumes, unites with 1 molecule or 2 unit volumes of chlorine, and forms 2 molecules or 4 unit volumes of hydrochloric acid: or again—

$$\mathrm{O_2 + 2H_2 = 2H_2O.}$$

One molecule, or 2 unit volumes of oxygen, unite with 2 molecules, or 4 unit volumes of hydrogen, and produce 2 molecules of water, which when vaporised, and measured under the same conditions of temperature and pressure, occupy 4 unit volumes. In

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[*] The number obtained by adding together the weights of the atoms in a formula is known as a "formula weight," thus 98 is the formula weight of sulphuric acid.

other words, the number of molecules, in all cases* where gases and vapours are concerned, represent exactly the volumetric relations. In the cases quoted, it will be observed, the same ratio also subsists between the number of *atoms* of the reacting gases and the molecules of the compound, but this is not always the case, for example—

Atomic equation, $Hg + 2Cl = HgCl_2$.

In this equation 3 atoms unite to produce 1 molecule, but the ratio between the volumes is *not* represented by the statement, 1 volume of mercury vapour and 2 volumes of chlorine produce 2 volumes of vapour of mercury chloride.

Molecular equation, $Hg + Cl_2 = HgCl_2$.

By this we see that 1 molecule† (2 unit volumes) of mercury vapour, and 1 molecule (2 unit volumes) of chlorine, give 1 molecule (2 unit volumes) of vapour of mercury chloride.

Again, $P + 3Cl = PCl_3$ is an atomic equation, showing that 1 atom of phosphorus unites with 3 atoms of chlorine; but it is *not* true that the ratio between the volumes is represented by the statement, 1 volume of phosphorus vapour combines with 3 volumes of chlorine, and gives 2 volumes of the vapour of phosphorus trichloride, as will be seen by comparison with the molecular formulæ—

$$P_4 + 6Cl_2 = 4PCl_3.$$

This equation tells us that 1 molecule‡ (2 unit volumes) of phosphorus vapour combines with 6 molecules (12 unit volumes) of chlorine, producing 4 molecules (8 unit volumes) of phosphorus trichloride vapour.

Knowing the relative densities of gases compared with hydrogen, it is obviously possible, by ascertaining the actual weight in grammes of some definite volume of hydrogen, to calculate the actual weight of any given volume of any other gas.

Two units are in common use, namely—

(I.) The weight of 1 litre of hydrogen, measured at a temperature of 0° C., and under a pressure of 760 mm. of mercury.§

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* See Dissociation, where apparent exceptions are explained.

† The atomic volume of mercury vapour being equal to 2 unit volumes (p. 43).

‡ The atomic volume of phosphorus is .5 of a unit volume (p. 43).

§ This temperature and pressure is chosen as the standard at which volumes of gases are compared. See General Properties of Gases, chapter ix.

(2.) The volume occupied by 1 gramme of hydrogen, measured under the same conditions.

I. One litre of hydrogen, measured at the standard temperature and pressure, weighs .0896 grammes.* This number is known as the *crith*;† and by means of it the weight of 1 litre, and therefore any given volume, of any gas can be deduced: thus, the relative densities of oxygen, nitrogen, and chlorine are 16, 14, and 35.5 respectively, therefore 1 litre of these gases (measured always at the standard temperature and pressure) weighs 16 criths, 14 criths, and 35.5 criths respectively, or—

1 litre of oxygen weighs 16 × .0896 = 1.4336 grammes.
1 „ nitrogen „ 14 × .0896 = 1.2544 „
1 „ chlorine „ 35.5 × .0896 = 3.1808 „

So also with reference to compound gases, where in each case the density is represented by the half of the molecular weight. Thus, the relative densities of hydrochloric acid, ammonia, and carbon dioxide are—

$$\mathrm{HCl}\ \frac{1 + 35.5}{2} = 18.25.$$

$$\mathrm{NH_3}\ \frac{14 + 3}{2} = 8.5.$$

$$\mathrm{CO_2}\ \frac{12 + 32}{2} = 22$$

and the weights of 1 litre of these gases are therefore—

1 litre of hydrochloric acid = 18.25 × .0896 = 1.6352 gramme.
1 „ ammonia = 8.5 × .0896 = 0.7610 „
1 „ carbon dioxide = 22.0 × .0896 = 1.9712 „

II. The volume occupied by 1 gramme of hydrogen at the standard temperature and pressure is 11.165 litres. As the relative density of oxygen is 16, it obviously follows that 16 grammes of this gas will also occupy 11.165 litres; in other words, this number 11.165 represents the volume in litres of any gas, which will be occupied by the number of grammes corresponding to its relative density, thus—

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* From time to time slightly different values have been given for this constant. The most recent determinations give the number .08988.

† From the Greek, signifying a barley-corn, and used symbolically to denote a little weight.

| | | | | | |
|---|---|---|---|---|---|
| 14 | grammes of | nitrogen . . | occupy | 11.165 | litres. |
| 35.5 | „ | chlorine . . | „ | 11.165 | „ |
| 18.25 | „ | hydrochloric acid | „ | 11.165 | „ |
| 22.0 | „ | carbon dioxide . | „ | 11.165 | „ |

The number of grammes of a substance, equal to the number which represents its molecular weight, is spoken of as the *gramme-molecule.* The molecular weight of hydrogen = 2, therefore the gramme-molecule of hydrogen (that is, 2 grammes of hydrogen) will occupy 11.165 × 2 = 22.33 litres. The molecular weight of oxygen = 32, therefore 32 grammes of oxygen will occupy 22.33 litres; in other words, 22.33 litres is the volume which will be occupied by the gramme-molecule of any gas.

By means of this important constant, 22.33, the volume of any, or all, of the gaseous products of a chemical change (when measured at the standard temperature and pressure) can be deduced directly from the equation representing the change, thus—

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

expresses the reaction taking place when zinc is dissolved in sulphuric acid. Just as in the former illustrations it carries the information that 65 grammes of zinc + 98 grammes of sulphuric acid produce 161 grammes of zinc sulphate and 2 grammes of hydrogen. But 2 grammes of hydrogen occupy 22.33 litres, therefore by the solution of 65 grammes of zinc, the volume of hydrogen obtained will be 22.33 litres.

So also in the following equation, which represents the formation of carbon dioxide from chalk (calcium carbonate) by the action upon it of hydrochloric acid—

$$\begin{array}{ccccccccc} CaCO_3 & + & 2HCl & = & CaCl_2 & + & H_2O & + & CO_2 \\ 40+12+48 & & 2(1+35.5) & & 40+71 & & 2+16 & & 12+32 \\ 100 & + & 73 & = & 111 & + & 18 & + & 44 \end{array}$$

100 grammes of chalk, when acted upon by 73 grammes of hydrochloric acid, yield 111 grammes of calcium chloride, and 18 grammes of water, and 44 grammes of carbon dioxide.

Carbon dioxide is gaseous, therefore 44 grammes (the gramme-molecule) will occupy, at the standard temperature and pressure, 22.33 litres; hence, by the decomposition of 100 grammes of chalk, 22.33 litres of carbon dioxide are produced.

This chapter may be concluded with one illustration of the methods employed in the exact determination of atomic weights, which depends essentially upon the quantitative character of chemical reactions. By the three following processes the atomic weights of chlorine, potassium, and silver may be deduced.

1. By heating a known weight of potassium chlorate, the formula weight of potassium chloride is found—

$$KClO_3 = KCl + 3O.$$

50 grammes of potassium chlorate when heated, left a residue of potassium chloride weighing 30.395 grammes. $50 - 30.395 = 19.605$ = grammes of oxygen evolved.

As potassium chlorate contains in its formula weight 3 atoms of oxygen ($16 \times 3 = 48$), we get the expression—

$$19.605 : 30.395 = 48 : 74.40 = \text{formula weight of potassium chloride.}$$

2. By dissolving a known weight of potassium chloride, and adding to it excess of silver nitrate, silver chloride is precipitated, which can be washed and dried and weighed, and from which the formula weight of silver chloride is obtained—

$$KCl + AgNO_3 = AgCl + KNO_3.$$

10 grammes of potassium chloride were found to yield 19.225 grammes of silver chloride; therefore,

$$10 : 19.225 = 74.40 : 143.03 = \text{formula weight of silver chloride.}$$

3. By the direct combination of silver and chlorine, by heating the metal in a stream of the gas, the ratio of chlorine to silver in silver chloride is found:

10 grammes of silver so treated yielded 13.285 grammes of silver chloride; therefore,

$$13.285 : 10 = 143.03 : 107.66 = \text{atomic weight of silver.}$$

Since the formula weight of silver chloride, $AgCl = 143.03$,

$$\text{therefore, } 143.03 - 107.66 = 35.37 = \text{atomic weight of chlorine.}$$

And since the formula weight of potassium chloride, $KCl = 74.40$,

$$\text{therefore, } 74.40 - 35.37 = 39.03 = \text{atomic weight of potassium.}$$

# CHAPTER VIII

## *VALENCY OF THE ELEMENTS*

WHEN chlorine unites with hydrogen, the combination takes place between one atom of chlorine (relative weight = 35.5), and one atom of hydrogen (relative weight = 1); but when oxygen combines with hydrogen, one atom of oxygen unites with *two* atoms of hydrogen. The compound ammonia consists of one atom of nitrogen, combined with *three* atoms of hydrogen; while one atom of carbon, on the other hand, can unite with *four* atoms of hydrogen.

One atom of chlorine never combines with more than one atom of hydrogen; its affinity for that element is satisfied, or *saturated*, by union with one atom.

The affinity of one atom of oxygen for hydrogen, however, is not satisfied by one atom of that element, but requires two atoms for its saturation; while nitrogen requires three, and carbon four hydrogen atoms, in order to satisfy their respective affinities for this element.

This varying power of combining with hydrogen is seen in a number of other instances: thus, the elements fluorine, bromine, and iodine, resemble chlorine in being only able to unite with one atom of hydrogen. Sulphur, like oxygen, has its affinity for hydrogen saturated by two atoms of that element. Phosphorus and arsenic require three atoms of hydrogen in order to saturate their combining capacity, while silicon resembles carbon in combining with four hydrogen atoms. This combining capacity of an element is termed its *valency*. Elements like chlorine, fluorine, bromine, and iodine, whose atoms are only capable of uniting with one atom of hydrogen, are called *monovalent* (or sometimes *monad*) elements; while those whose atoms combine with two, three, or four hydrogen atoms, are distinguished as di-valent (or dyad), tri-valent (or triad), and tetra-valent (or tetrad) elements. All elements, however, are not capable of entering into combination with hydrogen; in which case, their valency is measured by the number of atoms of some other monovalent element which is capable of satisfying their combining capacity. Thus:—

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1 | atom of | sodium | combines with | 1 | atom of chlorine, | forming | NaCl. |
| 1 | „ | calcium | „ „ | 2 | atoms „ | „ | $CaCl_2$. |
| 1 | „ | boron | „ „ | 3 | „ „ | „ | $BCl_3$. |
| 1 | „ | tin | „ „ | 4 | „ „ | „ | $SnCl_4$. |
| 1 | „ | phosphorus[*] | „ | 5 | „ „ | „ | $PCl_5$. |
| 1 | „ | tungsten | „ „ | 6 | „ „ | „ | $WCl_6$. |

In the combinations of elements with hydrogen alone, no instances are known in which a higher valency is exhibited than that of four; but with chlorine as here seen, cases are known in which elements exhibit pentavalent and hexavalent characters.

Measured by their combining capacity for hydrogen and chlorine, elements do not, however, always exhibit the same valency: thus, the affinity of phosphorus for hydrogen is satisfied by three hydrogen atoms, whereas one atom of this element can unite with five atoms of chlorine.

As measured by hydrogen, the valency of sulphur is two, the compound that it forms with hydrogen being expressed by the formula $SH_2$, while, as estimated by its capacity for chlorine, it becomes tetravalent, as seen in the compound $SCl_4$. As a general rule, however, the highest number of monovalent atoms with which one atom of an element is capable of combining, is accepted as representing the valency of that element. Thus, one atom of phosphorus not only combines with five atoms of chlorine, but also with five atoms of fluorine; phosphorus is therefore a pentavalent element.

As measured by hydrogen alone, or by chlorine alone, nitrogen is a trivalent element, for the largest number of these atoms with which one atom of nitrogen can unite is three, as seen in the compounds having the composition $NH_3$ and $NCl_3$; nevertheless, one atom of nitrogen is capable of combining with four atoms of hydrogen and one of chlorine, forming the compound $NH_4Cl$, ammonium chloride, in which the nitrogen atom is pentavalent.

This rule, however, is not always followed; for example, one atom of iodine will unite with three atoms of chlorine, forming the compound $ICl_3$, but iodine is not generally regarded as a trivalent element.*

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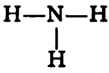
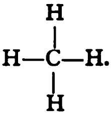
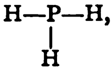
[*] Phosphorus also combines with hydrogen.

In symbolic notation, this power possessed by an atom, of uniting to itself monovalent atoms, is often represented by lines, each line signifying the power of combination with one monovalent atom. Thus, in the symbol H—Cl, the line is intended to give a concrete expression to the fact that both hydrogen and chlorine are monovalent elements, and that the affinity of each element for the other is satisfied, when one atom of the one, unites with one atom of the other. The symbol H—O—H, in like manner, signifies that the oxygen atom is divalent, that its affinity for hydrogen is satisfied only, when it has united with two monad atoms. In the same way we may express the facts that nitrogen and carbon, in their combinations with hydrogen, are respectively trivalent and tetravalent, by the symbols  $H-\underset{\underset{H}{|}}{N}-H$, and  $H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H$. These lines are merely a convenient symbolic expression for the operation of the force of chemical affinity; their length and direction bear no meaning.† The power to combine with one monovalent atom is sometimes spoken of simply as one *affinity:* thus it is said that in the compound having the composition $PH_3$, or  $H-\underset{\underset{H}{|}}{P}-H$, three of the *affinities* of the phosphorus atom are saturated, and that two *affinities* still remain unsatisfied, phosphorus, as already stated, being a pentavalent element.

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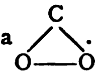
* See Iodine, Compounds.

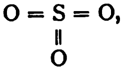
† The student cannot be too often warned against attaching any materialistic significance to these lines. The use of this convention is always attended with the danger that the beginner is liable to fall into the error of regarding these lines as representing in some manner fixed points of attachment, or links, between the atoms. It must be remembered, therefore, that these lines not only have no materialistic signification, but they must not even be regarded as conveying any statical meaning. The atoms are undergoing rapid movements with respect to each other, which movements are in some way governed by the chemically attractive force exerted by the individual atoms upon one another; and the molecule will be more correctly considered, if we regard its atoms as being held together in a manner resembling that by which the numbers of a cosmical system are bound together. The lines simply denote that the atoms *are held to* each other by the attractive force which we call chemical affinity.

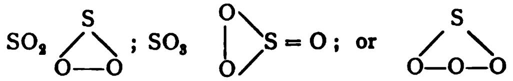
Compounds of this order, in which one of the elements has still unsatisfied affinities, are called *unsaturated* compounds.

In its power to satisfy the affinities of an element, a divalent atom is equal to two monovalent atoms: thus, when the affinities of the tetravalent carbon atom are saturated with oxygen, the molecule contains two atoms of oxygen, which may be symbolically expressed thus, $O = C = O$, in which the four affinities of the carbon (represented by the four lines) are satisfied by the two divalent atoms of oxygen. Carbon, however, combines with a smaller proportion of oxygen, forming the compound carbon monoxide, $CO$. The carbon atom in this case is divalent, as expressed by the formula $C = O$, and this substance is also an unsaturated compound.

The number of divalent atoms with which an element can unite, cannot, however, be taken as a safe criterion or measure of the atomicity of that element in cases where that number is greater than 1; for example, in such a compound as calcium oxide, $CaO$, we regard the two affinities of the divalent atom of oxygen as being satisfied by two affinities possessed by the calcium, and express this belief in the formula $Ca = O$, and regard the calcium as divalent. In the same way, in carbon monoxide, $CO$, the carbon being united with one atom of the divalent element oxygen, is itself divalent in this compound; but in the case of carbon dioxide, where the carbon atom is united with two atoms of divalent oxygen, we are not justified in asserting that the atoms are united, as represented by the formula $O = C = O$, in which the four affinities of carbon are represented as saturated with oxygen. There exists no positive proof that the carbon is not divalent in this compound, and that the molecule does not consist of three divalent atoms united, as shown in the formula . From the fact, however, that carbon forms a compound with four atoms of hydrogen, and another with four atoms of chlorine, we know that this element is tetravalent, and therefore we *believe* that in carbon dioxide it is also tetravalent.

Again, as measured by its compound with hydrogen, sulphur is divalent; while with chlorine it forms $SCl_4$. But sulphur unites with oxygen, forming the two compounds, sulphur dioxide $SO_2$ and sulphur trioxide $SO_3$. If it be assumed that in these molecules the whole of the oxygen affinities are satisfied with sulphur, then the symbolic representation of these oxides will be $O = S = O$, and $O = \underset{\underset{O}{\|}}{S} = O$, the sulphur being in one case tetravalent, and in the other hexavalent. There is, however, no *positive* proof that the affinities of one oxygen atom are not partially satisfied by union with another oxygen atom, and that the valency of the sulphur is higher than either two or four, as seen in the alternative formulæ,





Although there are no known compounds in which an atom of sulphur is united with six monovalent elements, sulphur is regarded by many chemists as capable of fulfilling the functions of a hexavalent element.

It will be evident from these considerations, that in many cases the valency of an element is a variable quantity, depending partly upon the particular atoms with which it unites. It is also found that it is dependent in many instances upon temperature and upon pressure. Thus, between a certain limited range of temperature, one atom of phosphorus combines with five atoms of chlorine in the compound $PCl_5$, but above that limit two atoms of chlorine leave the molecule, and the phosphorus becomes trivalent. Again, if phosphoretted hydrogen, $PH_3$, be mixed with hydrochloric acid, HCl, and the mixed gases be subjected to increased pressure, the gases combine and form a solid crystalline compound known as phosphonium chloride, $PH_4Cl$, in which the phosphorus atom, being united with five monovalent atoms, is pentavalent. When the pressure is released, an atom of hydrogen and an atom of chlorine leave the molecule, and the phosphorus returns to its trivalent condition.

A compound, in whose molecules there is an atom which for the time being is not functioning in its highest recognised valency, often exhibits a readiness to unite with additional atoms to form new compounds: thus, ammonia combines eagerly with hydrochloric acid, forming ammonium chloride—

$$NH_3 + HCl = NH_4Cl.$$

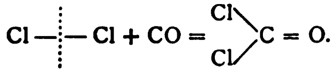
Carbon monoxide unites directly with chlorine to form carbonyl chloride—

$$CO + Cl_2 = COCl_2.$$

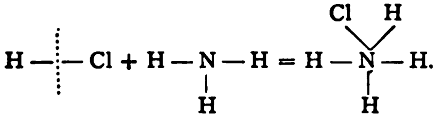
Carbon monoxide also combines with an additional atom of oxygen, and gives carbon dioxide, thus—

$$2CO + O_2 = 2CO_2.$$

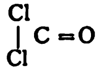
In this last action it will be seen that the molecule of carbon monoxide, in being converted into the dioxide, takes up one atom of oxygen; but as the molecule of oxygen is the smallest isolated particle, it follows that the two atoms contained in such a molecule must first separate, and each one then furnishes the requisite additional oxygen for one molecule of carbon monoxide. In the union of carbon monoxide with chlorine, and of ammonia with hydrochloric acid, are we to suppose that the same action takes place? That is to say, do the two atoms in the molecule of chlorine separate from each other and unite with carbon, thereby satisfying its tetrad valency, in the manner here expressed?—



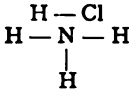
And in the case of ammonia and hydrochloric acid, do the hydrogen and chlorine atoms part, and each unite with the nitrogen atom, thereby raising it from the trivalent to the pentavalent condition? thus—



Or are we to suppose that the two molecules, without losing their integrity, become held together as independent molecules, by virtue of the unsatisfied affinities of the carbon, or the nitrogen, as the case may be, in which case the compounds might be represented thus—



$$\overset{Cl}{\underset{Cl}{|}}\;C=O$$



$$\begin{array}{c} H-Cl \\ H-N-H \\ | \\ H \end{array}$$

This question would be settled by determining the vapour density of the compound. If, for instance, we were to find the vapour-density of ammonium chloride to be 26.75, then the compound having the composition $NH_4Cl$ would have the normal molecular volume, that is, its molecule would occupy two unit volumes,* and the conclusion would be that the vapour consisted of single molecules of the composition represented by the formula $NH_4Cl$. But ammonium chloride at ordinary temperatures is a solid, and when heated to the temperature necessary to convert it into vapour its molecules break up into separated molecules of the two original gases—ammonia, $NH_3$, and hydrochloric acid, HCl.† So that we are unable to gain any information in this direction as to the mode in which the atoms are disposed in the compound. When the two gases are brought together under ordinary conditions, they combine with the evolution of considerable heat, owing to loss of energy; this is taken as evidence that true chemical action, in the sense of atomic rearrangement, has resulted, hence it is believed that in this compound the nitrogen is united with the five monovalent atoms, and consequently is pentavalent.

In the case of carbonyl chloride, $COCl_2$, the vapour-density can be ascertained, this compound existing in the gaseous condition at the ordinary temperature. Its vapour-density, determined by experiment, is found to be 50.6. This number, divided into the molecular weight of the compound having the composition $COCl_2$, gives practically the number 2 as the molecular volume of the compound. Hence we conclude that these four atoms constitute a single molecule.

There is a certain class of combinations, in which molecules of different compounds unite, that do not so readily admit of explanation, because in neither of the molecules is there any atom functioning in a lower state of valency than that which it is known to be capable of. For example, the monovalent elements, fluorine and hydrogen, form the compound hydrofluoric acid, HF; fluorine also combines with the monovalent element potassium, forming potassium fluoride, KF. Both of these compounds come under the head of *saturated* compounds, in the sense that neither of them contains an atom which is known to be capable of exercising a higher valency than it exhibits in these compounds. Nevertheless these two molecules unite together and form a definite chemical compound, known as hydrogen-potassium fluoride.

Again, the divalent element zinc combines with two atoms of the monad element chlorine, forming zinc chloride, $ZnCl_2$; the two monovalent elements, sodium and chlorine, also combine, giving the compound sodium chloride, NaCl. Both of these substances must be regarded as saturated compounds, and yet they unite with each other, forming a distinct chemical compound, known as sodium zinc chloride. Such compounds as these are known as *double salts*, and examples might be multiplied almost indefinitely. A similar union of molecules, where the recognised valency of the atoms is all satisfied, is seen in a large number of compounds containing water for crystallisation;* for example, the divalent element copper, in combination with two atoms of chlorine, forms cupric chloride, $CuCl_2$. The divalent element oxygen, in combination with two hydrogen atoms, forms water, $H_2O$. When cupric chloride crystallises from aqueous solution, each molecule of the chloride unites to itself two molecules of water, which is therefore termed water of crystallisation.

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* See p. 42.

† See Dissociation, p. 86.

In chemical notation, it is usual to represent compounds of this order, by placing the formulæ of the different molecules that have entered into union, in juxtaposition, with a comma between; accordingly, the examples here quoted would be indicated thus—

| | |
|---|---|
| Hydrogen potassium fluoride | HF,KF. |
| Sodium zinc chloride | $ZnCl_2,NaCl$. |
| Crystallised cupric chloride | $CuCl_2,2H_2O$. |

Combinations of this order are by no means confined to the union of *two* kinds of molecules, as the following examples will serve to show:—

| | |
|---|---|
| Platinum sodium chloride | $PtCl_4,2NaCl,6H_2O$. |
| Mercuric potassium chloride | $2HgCl_2,KCl,2H_2O$. |

At the present time our knowledge of the nature of the union between these various molecules is too imperfect to admit of any precise explanation; such compounds are frequently distinguished as *molecular combinations*.

It must be remembered that our ideas of valency are based mainly upon the consideration of matter in the gaseous state; at present we have little certain knowledge as to the valency of elements in liquid and solid compounds. Most of the compounds belonging to the class we are now discussing are solid, and it is quite conceivable that the valency of an element might increase, as the compounds in which it functions pass from the gaseous to the liquid and solid state.

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* *See p.* 192.

There is also another consideration that must not be overlooked. The unit of measure that has been adopted for estimating valency, namely, 1 monovalent atom, is probably only an extremely rough and crude measure, which is incapable of appreciating smaller differences of combining capacity that may, and most probably do, exist. Its use may be compared to the adoption of a single unit, say 1 gramme, for the estimation of mass, or weight; when, if a given quantity of matter has a weight equal to 1 gramme but less than 2 grammes, its weight would be 1; if greater than 2 grammes but less than 3, then its weight would be 2—a method of estimating which tacitly assumes that no intermediate weights of matter between the various multiples of the selected unit are possible. There is no evidence to show that the combining capacity of an element is *exactly* expressed by simple multiples of a monovalent atom.

For example, in the simplest form of combination, such as that between hydrogen and chlorine—where the molecule contains 1 atom of each element—1 hydrogen atom unites with 1 chlorine atom, that is to say, with a mass of chlorine weighing 35.5 times its own weight; and we say that the *mutual* affinities of these atoms are satisfied. But for anything we know to the contrary, an atom of hydrogen may have an affinity for chlorine which would enable it to unite with a mass of chlorine weighing 40 or 45 or 50 times its own weight, but *not* a mass weighing 71 (35.5 × 2) times its own. But since a mass of chlorine 35.5 times the weight of a hydrogen atom is the smallest quantity that is ever known to take part in a chemical change, is the chemically indivisible mass we call an atom, it follows that as the hydrogen atom has not sufficient combining capacity to unite with 2 atoms, it is compelled to be satisfied with 1. It might still, however, retain a *residual combining capacity*. Or the residual combining capacity may be lodged in the chlorine atom, which may be conceived as being able to unite with a greater weight of hydrogen than is represented by 1 atom, but not so much as that of 2 atoms.

Each of the elements fluorine, chlorine, bromine, and iodine unites with 1 atom of hydrogen, and we represent their compounds in a similar manner, thus:—

$$H-F; \quad H-Cl; \quad H-Br; \quad H-I;$$

but we make an enormous assumption if we suppose that in each of these compounds the mutual affinities of the atoms is equally satisfied.

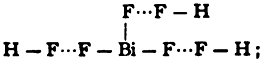
For example, the fluorine compound exhibits a tendency to unite itself to other compounds of fluorine (and to a much more marked degree than is seen in the case of hydrochloric acid), resulting in the formation of such double fluorides as the following:—

| | |
|---|---|
| Hydrogen potassium fluoride . . . . . | $KF,HF$. |
| Hydrogen bismuth fluoride . . . . . . | $BiF_3,3HF$. |
| Hydrogen silicon fluoride (Hydro-fluo-silicic acid) | $SiF_4,2HF$. |

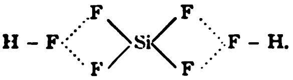
*And there is* reason for believing that the molecules of hydrofluoric acid are capable of uniting amongst themselves, forming the double molecule HF,HF.*

Assuming the residual combining power to reside in the fluorine atom, and representing this by means of dotted lines, we may express the composition of these compounds thus—

$$\mathrm{H - F\cdots F - H},$$



$$\mathrm{H - F\cdots F - \overset{\overset{F\cdots F - H}{|}}{Bi} - F\cdots F - H};$$



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* See Hydrofluoric acid.

# CHAPTER IX

## *GENERAL PROPERTIES OF GASES*

UNDER the head of the general properties of gases it will be convenient to consider the following subjects :[*]—

1. The relation of gases to heat.
2. The relation of gases to pressure.
3. The liquefaction of gases.
4. Diffusion of gases.
5. The kinetic theory of gases.

**The Relation of Gases to Heat.**—The fact that substances expand when heated, and again contract upon being cooled, was observed in very early times. The fact also that all substances do not undergo the same alterations in volume when subjected to the same changes of temperature has been long known ; but it was not until the beginning of the nineteenth century that it was proved by Charles and Gay-Lussac that all gases expanded and contracted equally when exposed to the same alterations of temperature. This law is generally known as the Law of Charles, and may be thus stated : *When a gas is heated, the pressure being constant, it increases in volume to the same extent whatever the gas may be.*

The increase in bulk suffered by 1 volume of a gas in being heated from 0° to 1° is termed the coefficient of expansion, and if the law of Charles is true all gases will have the same coefficient.

Modern research has shown that the law of Charles is not *absolutely* true, and the extent to which gases deviate from the strict expression will be seen from the coefficients of expansion given in the following table :—

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[*] The study of these subjects belongs more especially to the science of physics or chemico-physics. For fuller information on these points than can be included within the scope of this book students are referred to special treatises on physics.

| | |
|---|---|
| Air . . . . . . . . | .003665 |
| Hydrogen . . . . . . . | .003667 |
| Carbon monoxide . . . . | .003667 |
| Nitrogen . . . . . . . | .003668 |
| Nitrous oxide . . . . . | .003676 |
| Carbon dioxide . . . . . | .003688 |
| Cyanogen . . . . . . . | .003829 |
| Sulphur dioxide . . . . | .003845 |

It will be noticed that the first four gases have almost the same coefficient of expansion: these gases are all very difficult of liquefaction, and it will be seen that the coefficient rapidly rises in the case of the other gases, which are easily liquefied.

For purposes of ordinary calculation it is usual to adopt the coefficient of expansion of air, as applicable to all gases. It will be obvious that since the volume of a gas is affected by alterations of temperature, it becomes necessary, when measuring the volume of a gas, to have regard to the particular temperature at which the measurement is made, and in order to compare volumetric measures they must be all referred to some standard temperature. This standard temperature is by general consent 0° C.

Taking the fraction .003665 therefore for the coefficient—

1 volume of a gas at 0° becomes $1 + .003665$ volumes at 1°
1 „ „ 0° „ $1 + .003665 \times 2$ „ 2°
or 1 „ „ 0° „ $1 + .003665\,t$ „ $t°$

Therefore the volume at $t°$ equals the volume at 0° multiplied by $1 + .003665\,t$. Let $v$ be the volume at $t°$, and $v_0$ the volume at 0°, then—

$$v = v_0(1 + .003665\,t)$$

and conversely the volume at 0° equals the volume at $t°$ divided by $1 + .003665\,t$—

$$v_0 = \frac{v}{1 + .003665\,t}$$

The vulgar fraction equivalent to .003665 is $\frac{1}{273}$. 273 volumes at 0° become $273 + t$ at $t°$.

What is known as the *absolute temperature* of a substance is the number of degrees above −273° C. Taking this point as the zero, the absolute temperature of melting ice, *for* example, will be 273°. Charles' law, *therefore, may be thus stated: The volume of any* *gas, under constant pressure, is proportional to the absolute temperature.*

**The Relation of Gases to Pressure.**—The effect of increase of pressure upon a gas is to diminish its volume. The law which connects the volume occupied by a gas, with the pressure to which it is subjected was discovered by Robert Boyle (1661), and is known as Boyle's Law. It may be thus stated: *The volume occupied by a given weight of any gas is inversely as the pressure.* The general truth of this law may readily be illustrated by subjecting a gas to varying pressures, and it will be seen that when the pressure is doubled the volume of gas is reduced to one-half, and so on.

Just as in the case of the law of Charles, modern investigations have shown that the law of Boyle is not a mathematical truth. It is found not to be absolutely true of any gas, for with the exception of hydrogen, all gases are more compressible than is demanded by the law. Hydrogen deviates from the law in an opposite sense, in that it requires a higher pressure than the law would indicate, in order to reduce a volume of it to a given point. These deviations from Boyle's law are explained by the operation of two causes: first, the attraction exerted by gaseous particles upon each other; second, the fact that increased pressure diminishes the space *between* the molecules, and not the actual space *occupied by* the molecules of a gas. When the former cause predominates, the gas deviates from the law by being more compressible; in the case of hydrogen, the second cause operates more powerfully. (See Kinetic Theory of Gases.) For ordinary purposes of calculation the law of Boyle may be regarded as true.

As the volume of a given weight of gas is so intimately related to the pressure, and as the atmospheric pressure is variable, it becomes necessary, in all quantitative manipulation with gases, to know the actual pressure under which the gas is at the time of measurement, and to refer the volume to a standard pressure. The pressure that has been adopted as the standard is that of a column of mercury 760 mm. in height. (See Atmosphere.)

If $v$ equals the volume of gas measured at $p$ pressure, and $v_o$ the volume at the standard pressure, then

$$v_o = \frac{vp}{760}$$

In practice it is most usual to make both correction for tempe-pressure together; then $v_0$ being the volume at the nperature and pressure, we get

$$v_0 = \frac{v}{1 + .003665\,t} \cdot \frac{p}{760}{}^*$$

**efaction of Gases.**—Under certain conditions of tem- l pressure, the law of Charles and the law of Boyle both break down. According to Charles, 100 c.c. of a gas at occupy 96.4 c.c. if the tem- re lowered to − 10°. If 100 gas sulphur dioxide at 0° C. in a glass tube standing in d the gas be cooled to − 10° ing the tube with a freezing vill be found that the volume ead of occupying 96.4 c.c., duced to a few cubic centi- , and that the surface of the he tube is wet owing to the minute layer of a colourless it. In this case the law of broken down, and the sul- has passed from the gaseous state. according to the law of c.c. of a gas measured at the essure should occupy 25 c.c. ed to a pressure of four additional atmospheres. If e gas sulphur dioxide be enclosed in one limb of a long hown in Fig. 1, the other limb being filled with air, gases be simultaneously exposed to increased pressure he mercury reservoir, it will be seen that at first the th tubes are compressed equally. As the pressure three atmospheres, however, the mercury will be seen

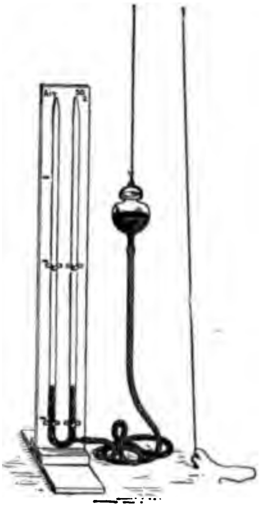

FIG. 1.

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ent should familiarise himself with the method of calculating the ume suffered by gases, by changes of temperature and pressure, it a number of examples such as the following:—

es of gas are cooled from 25° to 0°, what is the diminution in ressure being constant? *Ans.* 2.51 litres.

of air at 0° degrees weighs 1.~~239~~ grammes when the barometer to rise much more rapidly in the tube containing the sulphur dioxide, and when the mercury reservoir has been raised to such a height that the gases are subjected to four atmospheres, the sulphur dioxide will have completely broken down, and will be entirely converted into a few drops of liquid, which appear upon the surface of the mercury. The air meantime, in the other limb, will be found to occupy 25 c.c., as that gas at that pressure obeys Boyle's law almost absolutely. We see, therefore, that at a certain temperature and at a certain pressure the gas sulphur dioxide begins rapidly to depart from the laws of Charles and Boyle, and ultimately passes into the liquid condition.

All known gases, with the one exception of hydrogen, when exposed to certain conditions of temperature and pressure, conditions which are special for each different gas, will pass from the gaseous to the liquid state: and as the point at which liquefaction takes place is approached, the departures from Boyle's law become more and more pronounced.

The first substance, recognised as being under ordinary conditions a true gas, that was transformed into the liquid condition, was chlorine, which was liquefied in the year 1806 by Northmore. The true nature of this liquid was not understood until Faraday investigated the subject.

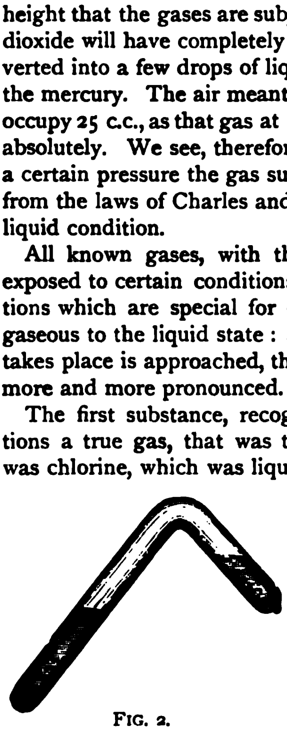

FIG. 2.

In his earlier experiments, Faraday's method consisted in sealing into a bent glass tube (Fig. 2) substances which, when heated, would yield the gas; the substances being contained in one limb of the tube, and the empty limb being immersed in ice. The pressure exerted by the gas thus generated in a confined space, was sufficient to cause a portion of it to condense to

is at 760 mm., what will be the weight of a litre of air at 27°, the barometer standing at the same height? *Ans.* 1.177 grammes.

3. What will be the weight of a litre of air at 42° when the barometer stands at 735 mm.? *Ans.* 1.084 grammes.

4. Air at a temperature of 15° is enclosed in a vessel and heated to 93°. Compare the pressure of the enclosed air with that of the atmosphere. *Ans.* As 61 : 48.

5. What will be the volume, at the standard temperature and pressure, of 500 c.c. of hydrogen, measured at 20°, and under a pressure of 800 mm.? *Ans.* .490 c.c.

ature and pressure together; then $v_0$ being the volume at the standard temperature and pressure, we get

$$v_0 = \frac{v}{1+.003665\,t} \cdot \frac{p}{760}\,^*$$

**The Liquefaction of Gases.**—Under certain conditions of temperature and pressure, the law of Charles and the law of Boyle both completely break down. According to the law of Charles, 100 c.c. of a gas at 0° C. should occupy 96.4 c.c. if the temperature were lowered to −10°. If 100 c.c. of the gas sulphur dioxide at 0° C. be confined in a glass tube standing in mercury, and the gas be cooled to −10° by surrounding the tube with a freezing mixture, it will be found that the volume of gas, instead of occupying 96.4 c.c., has been reduced to a few cubic centimetres only, and that the surface of the mercury in the tube is wet owing to the pressure of a minute layer of a colourless liquid upon it. In this case the law of Charles has broken down, and the sulphur dioxide has passed from the gaseous to the liquid state.

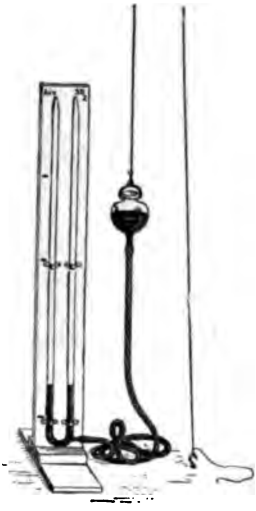

FIG. 1.

Similarly, according to the law of Boyle, 100 c.c. of a gas measured at the standard pressure should occupy 25 c.c. when exposed to a pressure of four additional atmospheres. If 100 c.c. of the gas sulphur dioxide be enclosed in one limb of a long U-tube, as shown in Fig. 1, the other limb being filled with air, and the two gases be simultaneously exposed to increased pressure by raising the mercury reservoir, it will be seen that at first the gases in both tubes are compressed equally. As the pressure approaches three atmospheres, however, the mercury will be seen

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* The student should familiarise himself with the method of calculating the changes of volume suffered by gases, by changes of temperature and pressure, by working out a number of examples such as the following:—

1. If 30 litres of gas are cooled from 25° to 0°, what is the diminution in volume, the pressure being constant? *Ans.* 2.51 litres.

2. If a litre of air at 0° *degrees weighs* 1.~~239~~ grammes when the barometer

gas to be liquefied is introduced into a glass tube (Fig. 3),
narrow end of which consists of a strong capillary tube. The t
carries a metal collar, which enables it to be secured in posit
in the strong steel bottle (Fig. 4), by means of a nut, E′ (Fig.
which screws into the mouth. The bottle, which is partially fil
with mercury, is connected, by means of a flexible copper tube
fine bore, with a small hydraulic pump, by means of which wa
is forced into the steel bottle. The water so driven in, forces

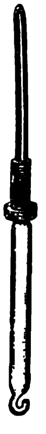

FIG. 3.

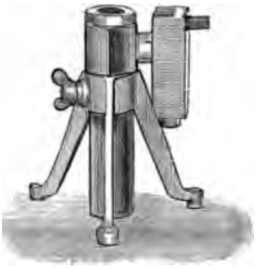

FIG. 4.

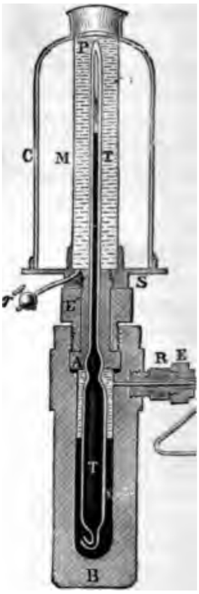

FIG. 5.

mercury up into the glass tube T, and thereby compresses
contained gas. In this way a pressure of several hundred atm
pheres may be applied to the gas. In his earlier experime
Cailletet depended almost entirely for the refrigeration he requir
upon the fact, that when a gas is allowed suddenly to expand
undergoes a great reduction in temperature. This method
cooling may be termed *internal* refrigeration. In the case
oxygen, the gas was first subjected to a pressure of 300 to

atmospheres, and was then allowed suddenly to expand by a rapid release of the pressure. The result of the sudden expansion was to momentarily lower the temperature of the gas to such a point that the tube was filled with a fog, or mist, consisting of liquid particles of oxygen.

In his more recent experiments Cailletet employed external refrigeration, and obtained oxygen in the form of a coherent liquid. Fig. 6 shows the essential parts of the apparatus. The capillary end O of the glass tube containing the gas, is bent as shown in the figure, so that the end of it can dip into the short glass tube F. The refrigeration is obtained by the evaporation of liquid ethylene, the supply of which is contained in the iron bottle E. This bottle is connected to a fine copper worm, A A′, contained in an inverted narrow glass bell, and which, after passing out through a cork at the base, is bent so as to deliver the liquid ethylene into the tube F. A second copper worm, B B′ is also contained in the bell; this is connected at B with a supply of hydrogen, while its lower extremity is connected to a glass tube, which also drops into F. The copper worms are cooled either by means of methyl chloride, or better, by a solution of solid carbon dioxide in ether, whereby the temperature of −70° is readily obtained. Liquid ethylene is then allowed to flow from the iron bottle through the cooled worm into the tube F, which, in order to prevent the condensation of hoar frost upon it, is enclosed in a glass jar, G, provided with a tight fitting cover, and containing a layer of sulphuric acid

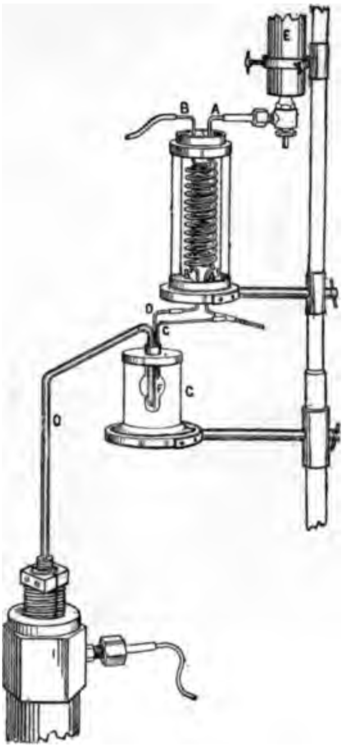

FIG. 6.

upon the bottom. A stream of dry hydrogen is then passed through the worm B B′, and this current of cold gas bubbling through the liquid ethylene in the tube F increases the rapidity of its evaporation to such an extent, that the temperature falls to about - 120°. At this temperature a pressure of about fifty atmospheres is sufficient to liquefy the oxygen, which collects in the end of the tube dipping into F as a colourless, transparent liquid.

By means of the refrigeration brought about by the rapid evaporation of liquid ethylene, oxygen may be liquefied in large quantities, and if collected in a glass vessel with double walls, the space between the walls being rendered perfectly vacuous, it may be preserved for a considerable time, as it is found that the vacuous envelope is the most perfect insulator.

Liquid oxygen itself may be employed as a still more powerful refrigerator: and by causing it to rapidly evaporate the temperature may be lowered to - 200°, when air itself liquefies without the application of any pressure. For this purpose a quantity of liquid oxygen is poured into the glass tube O (Fig. 7), which is provided with a vacuous envelope, V. Into this tube a cork is fitted, through which passes an empty test-tube, N, and a short tube, P, which can be put in connection with an exhaust pump. The liquid oxygen soon enters into rapid ebullition, and the temperature thereby becomes lowered to - 200°, when drops of liquid air begin to form upon the walls of the inner empty tube, and in a few minutes a considerable quantity of the liquid may be collected.

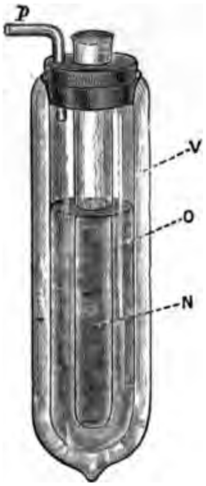

FIG. 7.

By means of these various methods all the difficultly condensed gases have been liquefied except hydrogen. It was at one time supposed that liquid hydrogen had been obtained, but further experiments have proved this not to have been the case, and up to the present time this gas has resisted all attempts to liquefy it. There is reason to believe that its liquefaction is an impossibility.

**The Critical Point.**—As far back as the year 1869, it was shown by Andrews that when liquid carbon dioxide was heated articular temperature, it passed from the liquid to the gaseous and that no additional pressure was able to condense it again g as the temperature remained at or above that point. This ular temperature is called the *critical point*, or the *critical rature* of the gas. In the case of carbon dioxide this critical rature is 31.9°, and in order that this gas may be liquefied by ure, it is an essential condition that the temperature be below point; above 32° no pressure is capable of bringing about action. All gases have a critical temperature, which is special ch gas, and until the temperature of the gas be lowered to point, liquefaction is impossible. The critical temperatures different gases vary through a very wide range, as will be from the following examples:—

| | |
|---|---|
| Nitrogen . . . . . . . | −146.0° |
| Carbon monoxide . . . . . | −140.0° |
| Oxygen . . . . . . . | −113.0° |
| Marsh gas . . . . . . . | − 99.0° |
| Ethylene . . . . . . . | + 10.1° |
| Carbon dioxide . . . . . . | 31.9° |
| Nitrous oxide . . . . . . | 35.4° |
| Acetylene . . . . . . . | 37.0° |
| Hydrochloric acid . . . . | 52.3° |
| Ammonia . . . . . . . | 130.0° |
| Chlorine . . . . . . . | 141.0° |
| Sulphur dioxide . . . . . | 155.4° |

e gases in this list, from ethylene downwards, all have their al temperatures so high, that there is no difficulty in cooling below these points. These are the gases which were first ed to the liquid state. The first four upon the list have low critical temperatures; these are the very gases which for ng resisted all attempts to liquefy them, and which were on account called *permanent* gases. We now know that the e to obtain them in the liquid state, was owing to the fact the relation between the critical temperature and the point uefaction was not fully realised. Just as carbon dioxide ot be liquefied unless its temperature be brought down to , so oxygen resists liquefaction under the highest possible ures, until its temperature be lowered to −113°, the critical erature of oxygen.

The critical temperature of a gas is sometimes spoken of as the *absolute boiling point.*

**Critical Pressure.**—The particular pressure that is required to liquefy a gas at its critical temperature, is called the *critical pressure.* Thus the pressure necessary to liquefy oxygen, when the temperature has been lowered to − 113°, is 50 atmospheres; while that required to condense chlorine at its critical point, viz., + 141°, is 84 atmospheres. Taken at their respective critical points, therefore, chlorine is a more difficultly liquefiable gas than oxygen, although at 0° chlorine is condensed by a pressure of only 6 atmospheres; 0°, however, is 141° below the *critical point* of chlorine, and it is more than probable that if it were possible to cool oxygen to a temperature 141° below *its* critical point, that is, to − 254°, it, in like manner, would be capable of liquefaction by very slight pressure.

**Diffusion of Gases.**—If a jar filled with hydrogen be placed mouth to mouth with a jar of air, the hydrogen being uppermost, it will be found that after the lapse of a few minutes some of the hydrogen will have passed into the bottom jar containing air, and some of the air will have made its way up into the hydrogen jar. The light gas hydrogen does not, as might have been supposed, remain floating upon the air, which is 14.44 times as heavy, but gradually escapes into the lower jar; and the heavier gas finds its way, in opposition to gravitation, into the upper jar. This process goes on until there is a uniform mixture of air and hydrogen in both jars, and the gases never separate again according to their densities.

This transmigration of gases will take place even through tubes of considerable length: thus, if two soda-water bottles be filled one with hydrogen, and the other with oxygen, and the two bottles be connected by a piece of glass tube a metre in length, the system being held in a vertical position with the light hydrogen uppermost, it will be found after an hour or two that the two gases have become mixed. Some of the hydrogen will have descended through the long tube into the lower bottle, and in like manner a portion of the oxygen, although nearly sixteen times as heavy as hydrogen, will have travelled up into the top bottle. That the gases have so mixed may be readily shown by applying a lighted taper to the mouth of each bottle, the detonation which then takes place proving that the bottles contained a mixture of oxygen and hydrogen. This passage of one gas into another is called the *diffusion of gases.* It was observed by Graham that when the ses were separated from each other by a thin porous such, for instance, as a piece of unglazed porcelain (so- 'biscuit"), or plaster of Paris, the pressure of the gas on sides of the porous partition did not remain the same he process of diffusion: that is to say, one gas made its ough the partition faster than the other, and it was noticed lighter the gas, the more rapidly was it able to transpire e through the porous medium. This fact, viz., that a light ses more rapidly than a heavier one, may be observed ety of ways.* The apparatus seen in Fig. 8 is a modified

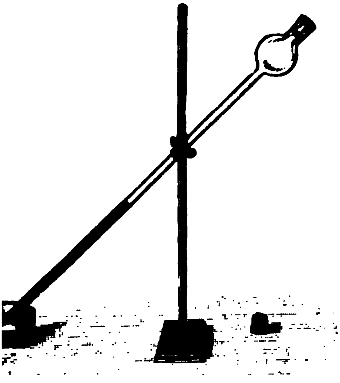

FIG. 8.

FIG. 9.

Graham's diffusiometer. It consists of a long glass tube enlargement or bulb near to one end. Into the short neck ulb there is fastened a thin diaphragm of stucco, or other naterial. If the apparatus be filled with hydrogen by dis- nt, the short neck being closed by a cork, and the long immersed in water, it will be seen, upon the withdrawal ork, that the water rapidly rises in the long tube. The n diffusing out through the diaphragm so much more than air can make its way in, a diminution in pressure

periments Nos. 335-344, *Newth's "Chemical* Lecture Experiments."

within the apparatus results, and this causes the water to ascend in the tube. The same phenomenon may be seen even more strikingly by means of the apparatus, Fig. 9, which consists of a tall glass U-tube, upon the end of one limb of which there is fastened, by means of a cork, a porous cylindrical pot, such as is used in an ordinary Bunsen battery. The U-tube is half filled with coloured water. Under ordinary circumstances air is continually diffusing through the porous pot, but as it passes at an equal rate in both directions, there is no disturbance of the pressure, and consequently the coloured water remains level in the two limbs. If now a beaker containing hydrogen be brought over the apparatus, as seen in the figure, the hydrogen will stream through the porous pot so much more rapidly than the air in the pot can make its way out, that there will be an increase in the total amount of gas inside the apparatus, which will be instantly rendered evident by the change of level of the liquid in the U-tube, the water being forcibly driven down the tube which carries the porous pot. Upon removing the beaker the reverse operation will at once take place; the hydrogen inside the apparatus now rapidly diffuses out, and much more quickly than air can pass in, consequently a reduction of pressure within the apparatus results, which is indicated by a disturbance of the level of the water in the tube, in the opposite direction to that which occurred at first.

**The Law of Gaseous Diffusion.**—Graham established the law according to which the diffusion of gases is regulated, and it may be thus stated: *The relative velocities of diffusion of any two gases are inversely as the square roots of their densities.*

The density of hydrogen being 1, that of air is 14.44, the velocity of the diffusion of hydrogen therefore, as compared with that of air, will be in the ratio of $\sqrt{14.44}$ to $\sqrt{1}$. $\sqrt{14.44} = 3.8$, $\sqrt{1} = 1$. Therefore hydrogen diffuses 3.8 times faster than air; or 3.8 volumes of hydrogen will pass out through a porous septum, while only 1 volume of air can enter.

If $d$ = the density of a gas, air being unity, and $v$ = the volume of the gas which diffuses in the same time as 1 volume of air, then

$$v = \sqrt{\frac{1}{d}}.$$

The following table gives in the last column, the results obtained by Graham, which will be seen to accord very closely with the calculated numbers demanded by the law of diffusion :—

| Name of Gas. | Density of Gas compared with Air = *d*. | $\sqrt{\frac{1}{d}}$ | Volume of Gas which Diffused in the same Time as one Volume of Air. |
|---|---|---|---|
| Hydrogen . . . . | 0.06926 | 3.7794 | 3.83 |
| Marsh gas . . . | 0.559 | 1.3375 | 1.344 |
| Carbon monoxide . . | 0.9678 | 1.0165 | 1.0149 |
| Nitrogen . . . . | 0.9713 | 1.0147 | 1.0143 |
| Oxygen . . . . | 1.1056 | 0.9510 | 0.9487 |
| Sulphuretted hydrogen . | 1.1912 | 0.9162 | 0.95 |
| Carbon dioxide . . . | 1.5290 | 0.8087 | 0.812 |
| Sulphur dioxide . . | 2.247 | 0.6671 | 0.68 |

The property of diffusion is sometimes made use of in order to separate gases, having different densities, from gaseous mixtures. This process of separation by diffusion is known as *atmolysis*. The principle may readily be illustrated by causing a mixture of oxygen and hydrogen, in proportion to form an explosive mixture, to slowly traverse tubes made of porous material, such as ordinary tobacco pipes. Two such pipes may be arranged as shown in Fig. 10, and the gaseous mixture passed through in the direction indicated by the arrow. On collecting the issuing gas over water in a pneumatic trough, it will be found to have so far lost the hydrogen, by diffusion through the tube, that a glowing splint of wood when introduced into it, will be re-ignited.

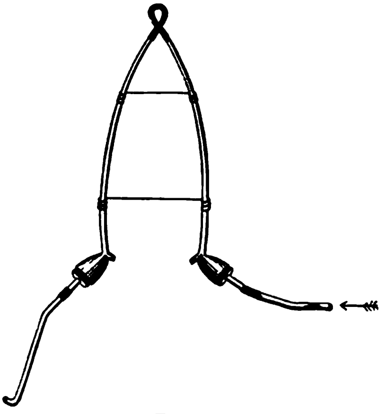

FIG. 10.

From the rate of diffusion of ozone, in a mixture of ozone and oxygen, Soret was able to calculate the density of this allotropic form of oxygen, and so confirm the result he had previously obtained by other methods (see Ozone).

Attempts have been made to utilise this principle in order to obtain oxygen from the air. The relative densities of oxygen and nitrogen are as 16 to 14; the rate of diffusion, therefore, of nitrogen is slightly greater than that of oxygen.

*Effusion* is the term applied by Graham to the passage of gases through a fine opening in a very thin wall, and he found that it followed the same law as diffusion. Bunsen utilised this principle for determining the density, and therefore the molecular weights, of certain gases. The method, in essence, is as follows:—A straight glass eudiometer is so constructed, that a gas contained in it can be put into communication with the outer air through a minute pin-hole in a thin platinum plate. The gas is confined in the tube, which is placed in a cylindrical mercury trough, by means of a stop-cock at the top. When the tube is depressed in the mercury, and the cock opened, the gas escapes through the minute perforation in the platinum plate, and its rate of effusion is determined by the time occupied by a glass float, placed in the tube, in rising a graduated distance within the eudiometer.

The flow of gases through capillary tubes is called *transpiration of gases*. In this case the friction between the gas and the tubes becomes a factor in the movement, so that this phenomenon is not governed by the same law as gaseous diffusion.

**The Kinetic Theory of Gases.**—The term *kinetic* signifies motion, and as applied to this theory it expresses the modern views of physicists concerning matter in the gaseous state, and serves to harmonise and explain the physical laws relating to the properties of gases. Matter in the state of gas or vapour, is regarded as an aggregation of molecules in which the attractive forces which tend to hold them together, are reduced to a minimum, and in which the spaces that separate them are at a maximum. These molecules are in a state of rapid motion, each one moving in a straight line until it strikes some other molecule, or rebounds from the walls of the containing vessel, when it continues its movement in another direction until it is once more diverted by another encounter. As they constantly encounter and rebound from each other, it will be evident that at any given instant some will be moving with a greater speed than others; the majority, however, will have an average velocity. In these encounters no loss of energy results so long as the temperature remains constant, but any change of temperature results in a change in the velocity of movement of the molecules, the speed being increased with increased heat. The actual volume of the molecules is very small as compared with the space occupied by the mass; the space between the molecules, therefore, in which they pass to and fro, is relatively very great. As the molecules are constantly colliding and rebounding, the distances between them, as well as their speed, will be sometimes greater and sometimes less; but there will be an average distance, which is known as the ***mean free path*** of the molecule.

The pressure exerted by a gas, or its elastic force, is the combined effect of the bombardment of its molecules against the containing vessel; in other words, the pressure of a gas is proportional to the sum of the products obtained by multiplying the mass of each molecule by half the square of its velocity. It will be obvious that if the space within which a given mass of gas is confined be reduced, the number of impacts of the molecules against the walls of the containing vessel, in a given time, will be increased, and therefore the pressure it exerts, or its elastic force, will also be increased. If the space be reduced to one-half the original, the number of these impacts will be doubled, or in other words, the number of impacts in a given time is inversely as the volume. This statement is simply the law of Boyle stated in the language of the kinetic theory.

When a given mass of gas contained in a confined space is heated, the pressure it exerts, or its elastic force, is increased. But as the number of molecules present has not been increased by raising the temperature of the gas (provided no chemical decomposition of the gas is brought about by the change of temperature), the increased pressure can only have resulted from the greater frequency, and greater energy, of the impacts of the molecules against the walls of the vessel, owing to their greater velocity.

Two equal volumes of different gases under the same conditions of temperature and pressure, exert the same elastic force upon the containing vessels, that is to say, the kinetic energy in each volume is the same. According to Avogadro's hypothesis, equal volumes of all gases under the same conditions of temperature and pressure, contain an equal number of molecules, however much the weight of these molecules may vary; therefore the average kinetic energy of each individual molecule will be the same. It follows from this that the mean velocities of different molecules must vary, and the calculated numbers representing the actual velocities of movement of the molecules of different gases, show that these rates are proportional to the inverse square roots of their respective densities. But according to the law of gaseous diffusion (Graham's law), the relative rapidity of diffusion of gases is inversely proportional to the square roots of their densities, hence by purely mathematical processes, based upon the kinetic theory of gases, the law of gaseous diffusion is proved to be true.

The deviations from the laws of Boyle and Charles, already referred to,* are also explained by the dynamical theory of gases, from considerations of the following order:—

1. That the molecules themselves are not mathematical points, but occupy a space; in other words, the space occupied by the actual particles of matter is not *infinitely* small as compared with the entire volume of the gas, *i.e.*, the bulk of the particle *plus* the intermolecular spaces.

2. That the impact of the molecules against each other and against the containing envelope occupies time; or, in other words, the time occupied by the impacts is not *infinitely* small compared with the time elapsing between the impacts.

3. That the molecules themselves are not entirely without attraction for each other; that is to say, although the attractive force between the molecules which holds them together in the liquid and solid states of matter, is at a minimum in the case of gases, it is not *entirely* absent.

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* See page 70.

# CHAPTER X

## *DISSOCIATION*

**Dissociation** is the term employed to denote a special class of chemical decompositions. When potassium chlorate is heated it breaks up into potassium chloride and oxygen, thus—

$$2KClO_3 = 2KCl + 3O_2,$$

and when calcium carbonate (chalk) is heated it breaks up into calcium oxide (lime) and carbon dioxide—

$$CaCO_3 = CaO + CO_2.$$

In the first case the oxygen is incapable of reuniting with the potassium chloride, but in the second, the carbon dioxide can recombine with the lime and reproduce calcium carbonate; therefore both the following expressions are possible—

$$CaCO_3 = CaO + CO_2,$$

and

$$CaO + CO_2 = CaCO_3.$$

Reactions of this order are known as *reversible* reactions, and the breaking up of calcium carbonate by the action of heat is termed dissociation, while that of the potassium chlorate under similar circumstances is simple decomposition.

When ammonia is passed through a tube heated to a dull red heat, the gas is *decomposed* into nitrogen and hydrogen—

$$2NH_3 = N_2 + 3H_2,$$

and the two gases pass out of the heated tube as separated gases, and do not recombine again.*

But when steam is strongly heated it is *dissociated* into oxygen and hydrogen, and as these separated gases pass away from the heated region they reunite, forming molecules of water vapour. Such a reversible reaction may be thus expressed—

---

* Nitrogen and hydrogen can be caused to unite under suitable conditions. See Ammonia.

$$2H_2O \rightleftarrows 2H_2 + O_2.$$

Again, when the gases ammonia and hydrochloric acid are brought together at the ordinary temperature, they unite to form solid ammonium chloride, and when ammonium chloride is heated it dissociates into its two generators,* hence we have the expression—

$$NH_3 + HCl \rightleftarrows NH_4Cl.$$

The corresponding compound containing phosphorus in the place of nitrogen, dissociates at a temperature as low as $-20^\circ$, hence when phosphoretted hydrogen and hydrochloric acid are mixed at ordinary temperatures no combination takes place, the separate molecules are in the same relation to one another as those of ammonia and hydrochloric acid at a *high* temperature. When, however, the mixture of gases is cooled below $-20$, union takes place and crystals of phosphonium chloride are formed, which at once begin to dissociate into the original gases as the temperature again rises. The change, as before, may be represented as a reversible one—

$$PH_3 + HCl \rightleftarrows PH_4Cl.$$

In such cases of dissociation as that of calcium carbonate, where one of the products is gaseous and the other solid, no difficulty exists in separating the simpler compounds that result from the decomposition ; but where the products are entirely gaseous, special methods have to be adopted to withdraw the one from the other, while they still exist as separate molecules, and before they reunite again. One such method, which is well adapted for the qualitative illustration of dissociation, is based on the law of gaseous diffusion. If when ammonium chloride is heated it is dissociated into ammonia, $NH_3$, and hydrochloric acid, $HCl$, these two gases, having the relative densities of 8.5 and 18.25, will diffuse through a porous medium at very different rates. According to the law of diffusion, these rates will be inversely as the square roots of the densities of the gases ; if therefore the conditions are so arranged

* Baker has shown (May 1894) that when *absolutely* dry, these gases do not combine ; and also, that when aqueous vapour is *entirely* absent, ammonium chloride does not undergo this dissociation.

that the heating of the ammonium chloride takes place in the neighbourhood of a porous diaphragm, more of the light ammonia gas will diffuse through in a given time, than of the heavier hydrochloric acid, so that a partial separation of these gases will be effected. Fig. 11 shows a convenient arrangement for carrying out the experiment. A fragment of ammonium chloride is heated in a short glass tube, through which passes the stem of an ordinary clay tobacco pipe. As the dissociation takes place, both of the gaseous products begin to diffuse into the interior of the porous clay pipe, but owing to their greater rate of diffusion, a larger number of ammonia molecules will pass in, than of hydrochloric acid, in the same time; consequently, when the gases pass away from the heated region and once more recombine, there will be a surplus of ammonia molecules within the porous pipe, and for the same reason an excess of hydrochloric acid molecules outside. If the gaseous contents of the porous tube be driven out by means of a stream of air from an ordinary bellows, the presence of the free ammonia may be recognised by allowing the air to impinge upon a piece of paper, coloured yellow with turmeric, which is instantly turned brown by ammonia. The excess of hydrochloric acid within the glass tube may also be proved, by placing a piece of blue litmus paper in the tube before heating the compound, and it will be reddened by the free hydrochloric acid.

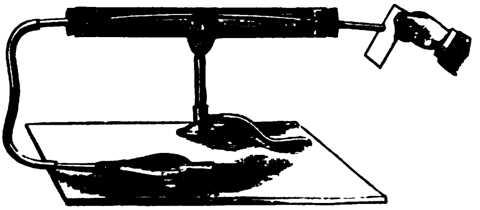

FIG. 11.

In all cases of dissociation, we may imagine two opposing forces in operation, one being the external force supplying the energy which tends to bring about the disruption of the molecules, and the other being the force of the chemical affinity existing between the disunited portions of the molecule, which tends to bring about their reunion. When these forces are equally balanced, the same number of molecules are dissociated as are recombined in a given unit of time, and the system is said to be in a state of equilibrium. If by any means the balance between the two opposing forces is disturbed, by augmenting or lessening either one or the other of them, the equilibrium of the system will also be disturbed and a new condition of equilibrium will be set up, in which again an equal number of molecules undergo dissociation and combination in a given time, but in which the ratio of the number of united and disunited molecules is different from that which obtained under the former condition of equilibrium. The relation between these two forces may be most readily disturbed, by either a change of temperature or pressure. Thus, in the case of nitrogen peroxide, $N_2O_4$, when this gas is at a temperature of 26.7°, 20 per cent. of it is dissociated into molecules having the composition $NO_2$; and so long as this temperature is maintained this ratio of the weight of the dissociated molecules to the total weight of the system (known as *the fraction of dissociation*) still subsists.

When the temperature of the gas is raised to 60.2°, the state of equilibrium existing at the lower temperature is disturbed, and the system gradually assumes a new condition of equilibrium, where once more the actual number of molecules undergoing dissociation and recombination in a given unit of time is the same, but where the percentage of dissociated molecules in the gaseous mixture is now 52.04.

It might at first be supposed that when such a gas is heated, and a temperature is reached at which the molecules are dissociated, that they would *all* dissociate, and that the process once begun would rapidly proceed until the decomposition was complete; instead of which, we find a definite fraction of dissociation corresponding to a particular temperature. This may be explained on the basis of the kinetic molecular theory. Let us imagine the gas nitrogen peroxide to be at a temperature below that at which dissociation begins, when all the molecules will have the composition $N_2O_4$. The molecules of the gas are in a state of rapid movement, and the rapidity of their movement is increased by rise of temperature. But the molecules in a given volume of the gas do not all move at the same velocity, and therefore they have not all the same temperature. On account of the infinite complications in their movements caused by their impacts against one another, some will be moving at a speed considerably greater than that of the average, and will have a temperature proportionally higher, while others again will have a velocity and a temperature below the average.

The observed temperature of the gas, therefore, is not that of the molecules having the highest or the lowest velocity and temperature, but is the average or mean temperature between, possibly, a very wide range.

On the application of heat to the gas, the observed or mean temperature rises, but the velocity of some of the molecules, and consequently their temperature, may have been thereby raised to the point at which dissociation takes place, and they consequently separate into the simpler molecules. Let us suppose that the observed temperature of the nitrogen peroxide is 26.7°, and that it is maintained at this point. Although this temperature may be below the dissociation temperature of the molecules, it must be remembered that it only represents the *mean* temperature, and that while some of the molecules have a lower, some also have a higher temperature. As already mentioned, at the temperature of 26.7°, 20 per cent. of the molecules are dissociated; that is to say, at any given instant one-fifth of the total number of molecules reach a velocity which causes them to break down into the simpler $NO_2$ molecules, which themselves then take up independent movements. If, in the process of their movements, two of these disunited molecules come into contact with each other at a moment when their velocities are lower than that at which they dissociated, they at once reunite, so that at the same instant some are uniting and others are dissociating, and, the two processes going on equally, the percentage of disunited molecules at any moment is the same, although the actual molecules which are dissociated at one point of time may not be the identical ones that are in this state at another time. Let us now suppose the gas to be heated until the registered (*i.e.*, the mean) temperature reaches 60.2°, and that it be maintained at this point. At this higher temperature a much larger proportion of the molecules will acquire a velocity at which they are unable to hold together, namely, 52.04 per cent.; but the remainder, amounting to nearly one-half, still are at a temperature below that at which dissociation takes place. Under these altered conditions a greater number of disunions and reunions takes place during a given interval of time, but the numbers are equal, and therefore the equilibrium exists. If once more the gas be further heated, until the indicated temperature is 140°, then it is found that the whole of the $N_2O_4$ molecules have dissociated into $NO_2$ molecules; that is to say, when the mean temperature has reached 140$^{c}$, then even those molecules that are moving with the slowest speed, have reached the temperature of dissociation. It will be evident that the rate at which the fraction of dissociation increases, as the temperature of a gas is gradually raised, will be greatest when the mean temperature approaches the *real* dissociation temperature of the gas, for the temperature of the greater number of the molecules will be coincident with, or very closely approximating to, that point.

The vapour density of nitrogen peroxide, if it could be ascertained when all the gaseous molecules had the composition $N_2O_4$, would be 46; while that of the gas, when entirely dissociated into $NO_2$ molecules, is 23. At temperatures between these extremes, the gas, consisting of mixtures of both molecules, will have a density lying between these figures, thus at 27.6° and 60.2° the density is 38.3 and 30.1 (see Nitrogen Peroxide, and also Phosphorus Pentachloride).

The effect of increased pressure upon a gas being to diminish the mean free path of the molecules, and thereby increase the number of molecules in a given space, the number of impacts between the molecules in a given time will be increased. If, therefore, while the nitrogen peroxide is maintained at a constant temperature, say 62.2°, the pressure be increased, the dissociated molecules, having shorter distances to travel, and making more frequent impacts in a given time, will unite more quickly than others are being disunited, and a fresh condition of equilibrium will be established for any particular pressure.

The case of phosphonium chloride already mentioned, may be referred to as an illustration. This compound is completely dissociated into molecules of phosphoretted hydrogen, $PH_3$, and hydrochloric acid, below a temperature of 0°. If, while at this temperature, it be subjected to pressure, the dissociated molecules are caused to unite, and at a pressure of thirteen atmospheres the union is complete, the whole of the disunited molecules having combined to form molecules of phosphonium chloride, $PH_4Cl$.

# CHAPTER XI

## *ELECTROLYSIS*

If a strip of pure zinc, and a strip of platinum, be together dipped into a vessel containing dilute sulphuric acid, neither metal is affected by the acid, so long as the metals do not touch each other. If the ends of the strips outside the liquid be joined by means of a metal wire, the zinc gradually dissolves in the acid, and bubbles of hydrogen are disengaged from the liquid in contact with the surface of the platinum plate (which itself is otherwise unaffected by the acid), and at the same time an electric current passes through the wire. So long as the chemical action of the sulphuric acid upon the zinc proceeds, so long will the electric current continue to pass; in other words, chemical energy will be transformed into electrical energy. If the wire be severed, the electric current can no longer pass, and the chemical action at once stops.

Such an arrangement constitutes a galvanic or voltaic element, or cell, and a series of such cells forms a galvanic battery. The zinc plate, or the end of a wire that may be connected to it, is termed the negative pole of the battery, while the end of a wire attached to the platinum plate is the positive pole. Other arrangements can be employed for generating a galvanic current, but in all cases the electrical energy is derived from chemical action.

If the two poles of a battery are connected together by placing them both in contact with various different substances, it is seen that in some cases the electric current passes, and in others not. For instance, if the poles are joined by placing them both in contact with a bar of sulphur, no current passes, whereas when connected by a rod of graphite the current freely passes. Substances which behave in this respect like the sulphur, are said to be non-conductors of electricity, while those that allow the current to pass, are distinguished as conductors. Substances capable of conducting electricity are of two kinds, namely, those which are merely heated, and those which undergo a chemical change, in consequence. All the metals, and a few of the non-metals, belong to the first of these classes; while the second includes a large number of compound substances, which are either in the liquid state, or in solution in some solvent. Thus, if the poles of a battery are immersed in pure water, practically no current passes, because this liquid is a non-conductor; but if a quantity of hydrochloric acid ($HCl$) be dissolved in the water, the solution at once becomes a conductor, and it is seen that gas is disengaged from the liquid upon the surface of each wire. Upon examination it is found that the gas evolved at the negative pole is hydrogen, while that from the positive pole is chlorine: the hydrochloric acid, therefore, is separated into its elements by the passage of an electric current through its aqueous solution. Such a process of decomposition is termed ***electrolysis***; and the conducting liquid is known as an ***electrolyte***.

The poles that are introduced into the electrolyte are called ***electrodes***, the negative electrode being sometimes termed the ***cathode***, and the positive electrode the ***anode***.

In a great number of instances, the electrolytic decomposition is accompanied by certain secondary reactions, caused by the action of the primary products of the decomposition upon either the electrolyte or the solvent; for example, when a solution of sodium chloride ($NaCl$) is electrolysed, the primary products are sodium and chlorine, the latter appearing at the anode and the sodium making its appearance at the cathode. The metal sodium, however, in contact with the water in the neighbourhood of the cathode, at once exerts chemical action upon the liquid, with the liberation of its equivalent of hydrogen, according to the equation—

$$Na + H_2O = NaHO + H.$$

In the same way, when an aqueous solution of copper sulphate ($CuSO_4$) is submitted to electrolysis, the primary products are copper, $Cu$, and the group $SO_4$. The copper is liberated at the cathode, and is deposited as a metallic film upon the electrode.[*]

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[*] This is the essence of the process of electro-plating. The metal to be deposited, whether it be gold, silver, or nickel, &c., in the form of a suitable salt (usually a double cyanide) in aqueous solution, forms the electrolyte. The object to be plated is made the cathode, that is, it is suspended in the liquid and is connected to the negative electrode of a suitable battery. The anode consists of a strip of the metal to be deposited. Thus in silver plating, a strip of silver is employed, and in this way the acidic radical that is liberated at the anode dissolves the metal, and thereby prevents the weakening of the solution, which would otherwise result from the gradual deposition of silver upon the cathode.

The group consisting of $SO_4$ passes to the anode, where it undergoes decomposition in the presence of the water, whereby ultimately oxygen is evolved and sulphuric acid produced—

$$SO_4 + H_2O = H_2SO_4 + O.$$

The primary products of electrolysis are termed the *ions*. Those ions that appear at the anode (positive electrode) are those which are negatively electrified, or which convey negative electricity; such as the elements fluorine, chlorine, bromine, iodine, and a number of acidic groups, or radicals, such as the $SO_4$ group already mentioned. Inasmuch as the negative ions appear at the anode, they are sometimes spoken of as *anions*.

Those ions, such as hydrogen and the metals, which travel to the cathode (negative electrode) are those that are positively electrified, or in other words, which convey positive electricity: positive ions, therefore, are distinguished as *cathions*.

**Faraday's Law.**—When the same quantity of electricity is passed through different electrolytes, the ratio between the quantities of the liberated products of the electrolysis, is the same as that between their chemical equivalents.

Thus, if the two electrolytes, hydrochloric acid and dilute sulphuric acid, be introduced into the same electric circuit, hydrogen and chlorine are evolved in the one case, and hydrogen and oxygen in the other. If the gases be all collected in separate measuring vessels, it will be seen (1) that the hydrogen and chlorine evolved from the hydrochloric acid are equal in volume; (2) that the volume of hydrogen collected from the other electrolyte is the same, while that of the oxygen is equal to only one-half this amount. Knowing the relative weights of equal volumes of these three gases to be hydrogen, oxygen, chlorine, as 1, 16, 35.5, we see that they must have been liberated in the proportions by weight of—

Hydrogen = 1 Oxygen = 8 Chlorine = 35.5.

Similarly, if the same quantity of electricity be passed through aqueous solutions of hydrochloric acid ($HCl$), silver nitrate ($AgNO_3$), copper sulphate ($CuSO_4$), and gold chloride ($AuCl_3$), by the time that 1 gramme of hydrogen has been liberated from the hydrochloric acid, there will be deposited upon the cathodes of the other electrolytic cells, 108 grammes of silver, 31.7 grammes of copper, and 65.6 grammes of gold. These numbers, which are the electro-chemical equivalents, are identical with the chemical equivalents of those elements, the chemical equivalent of an element being its atomic weight divided by its valency.

| | H. | O. | Cl. | Ag. | Cu. | Au. |
|---|---|---|---|---|---|---|
| Atomic weights . . | 1 | 16 | 35.5 | 108 | 63.5 | 197 |
| Valency . . . . | 1 | 2 | 1 | 1 | 2 | 3 |

Regarding the quantity of electricity required to liberate 1 gramme of hydrogen as the unit, we may say that 16 grammes of oxygen require 2 units of electricity for its liberation, 108 grammes of silver 1 unit, 63.5 grammes of copper 2 units, and 197 grammes of gold 3 units; or, in other words, the number of units of electricity required to liberate a gramme-atom, is identical with the number representing the valency of that atom in the particular electrolyte employed.

Some metals, such as copper, mercury, tin, &c., are capable of functioning with different degrees of valency. Thus copper is divalent in copper sulphate and in cupric chloride, but monovalent in cuprous chloride. If, therefore, 1 unit of electricity be passed through aqueous solutions of each of these copper chlorides, in the case of cupric chloride $\frac{63.5}{2} = 31.7$ grammes of copper will be deposited, while in the cuprous chloride $\frac{63.5}{1} = 63.5$ grammes are formed.

The modern theory now generally held, to explain the phenomena of electrolysis, is known as the theory of *electrolytic dissociation*. The passage of electricity through conductors of the two classes above mentioned, that is, through conductors such as metals, and those which are electrolytes, may be compared with the two ways by which heat is transmitted, namely, by conduction and convection. When a bar of metal is heated at one end, the heat travels along the bar, the metal remaining stationary; but when water is contained in a tube which is heated at its lower end, the heated particles of water travel along the tube, conveying the heat to the other extremity. In a similar manner, when electricity passes through a metallic conductor, the electricity travels through, or along, the metal, which itself does not move; but when it is passed through an electrolyte, it is conveyed, or transported, through the liquid by the moving ions. One set of ions charged with negative electricity travels towards the anode, while another set conveying positive electricity moves towards the cathode. In the earlier stages of the development of the present theory, it was supposed that the electrolyte was only separated into its ions as the electric current was passed into it, that the electricity was the prime cause of the dissociation of the electrolyte, hence the expression *electrolytic decomposition*, still commonly used. If this were in truth the case, it ought to be made manifest by the fact, that the electric current would have to do work in effecting such decompositions; but exact experiment goes to show that electricity is conducted with equal freedom by electrolytes as by metals. The theory proposed by Arrhenius (1887) is that a certain proportion of the molecules of the electrolyte are in a dissociated condition at all times. When, for example, sodium chloride is dissolved in water, some of the molecules, owing to their collisions, become separated into the ions, sodium and chlorine, much in the same way as a certain proportion of the molecules of a gaseous compound may be dissociated, and that these convey the electricity as soon as the electrodes are introduced into the solution.

From a number of other considerations, it is now believed that in such a saline solution the greater proportion of the compound is in the dissociated or disunited condition; the proportion depending largely upon the state of dilution. The more dilute the solution, and the more complete is the dissociation. At first it might appear contrary to established ideas, that in the case, for example, of such a compound as sodium chloride, the sodium and chlorine in the free state should be capable of existence in the same liquid; a liquid, moreover, upon which one of the elements, namely sodium, is under ordinary circumstances capable of exerting a chemical action. According to the electrolytic dissociation theory, however, the disunited constituents of the sodium chloride exist as separate atoms, having enormous electrical charges, the sodium with positive and the chlorine with negative electricity. Whenever the chlorine atoms lose their electrical charge, they unite together, forming the chlorine molecule $Cl_2$, which then possesses the properties which are usually associated with this element; and in the same way when the positively electrified sodium atoms give up their charge they likewise unite, forming sodium molecules, which are endowed with the ordinary properties belonging to that element. When the electrodes of a galvanic battery are placed into such a solution of sodium chloride, the negatively charged chlorine atoms travel to the anode, and there discharge their electricity, and in consequence, the chlorine atoms at that point unite, and molecules of ordinary chlorine escape as gas from the liquid. The sodium atoms with their positive charge travel to the cathode, where in like manner they are discharged, and at once unite to form sodium molecules, having the ordinary properties of sodium, and consequently at that point this element exerts its chemical action upon the water and liberates hydrogen.

This theory, that electrolytes in dilute solution are dissociated into their ions, is in harmony with, and derives support from, the laws which regulate the influence of substances in solution, upon osmotic pressure (page 136), upon the lowering of the vapour-pressure (page 118), and upon the lowering of the solidifying point of the solvent (page 121). Dilute solutions of electrolytes (strong acids, bases, and salts) exhibit deviations from these laws, much in the same way that gases which undergo dissociation, depart from the ordinary gaseous laws. It is found that in the case of dilute solutions of electrolytes, the osmotic pressure, the lowering of the vapour pressure, and the lowering of the freezing-point of the solvent, instead of being proportional to the number of *molecules* of the dissolved substance, are proportional to the number of *dissociated ions;* each ion behaving as a separate molecule.

# CHAPTER XII

## CLASSIFICATION OF THE ELEMENTS

s already been mentioned (page 7), that the elements may ıssified under the two subdivisions, *metals* and *non-metals.* er classifications have from time to time been in use, based other properties, such, for example, as the valency of the nts.

ssified according to their valency, the elements fall into six visions, consisting of mono-, di-, tri-, tetra-, penta-, and hexat elements. This system of classification has now largely into disuse, owing partly to the difficulties arising out of the oility of valency so often exhibited, but more especially to the recent development of another system, known as the *natural fication of the elements*, or the *periodic system*, which practiabsorbs and includes the older method.

rtain remarkable numerical relations have long been observed :ist among the atomic weights of elements that closely re- ıle one another in their chemical habits. In such groups milies it is frequently seen that the atomic weight of one ber, is approximately the arithmetic mean of the atomic hts of those immediately before and after it, when they are ıged in order of their atomic weights. This will be seen from ollowing examples :—

| | | | |
|---|---|---|---|
| Li.<br>7 | Na.<br>23 | K.<br>39 | $\frac{7 + 39}{2} = 23$ |
| K.<br>39 | Rb.<br>85 | Cs.<br>133 | $\frac{39 + 133}{2} = 85.8$ |
| P.<br>31 | As.<br>75 | Sb.<br>120 | $\frac{31 + 120}{2} = 75.5$ |
| S.<br>32 | Se.<br>79 | Te.<br>125 | $\frac{32 + 125}{2} = 78$ |

If the elements in these various families are so arranged, as to bring out the differences between their atomic weights, the striking fact will be observed that the increase in the atomic weights in each group takes place by practically the same increment. In the following table the elements belonging to the same group are placed in vertical columns, the differences between the various atomic weights being placed between them :—

| | | | | |
|---|---|---|---|---|
| F = 19 | N = 14 | O = 16 | Na = 23 | Mg = 24 |
| Difference . 16.5 | Diff. . 17 | Diff. . 16 | Diff. . 16 | Diff. . 16 |
| Cl = 35.5 | P = 31 | S = 32 | K = 39 | Ca = 40 |
| Difference . 44.5 | Diff. . 44 | Diff. . 47 | Diff. . 46.2 | Diff. . 47.3 |
| Br = 80 | As = 75 | Se = 79 | Rb = 85.2 | Sr = 87.3 |
| Difference . 47 | Diff. . 45 | Diff. . 47 | Diff. . 47.8 | Diff. . 49.7 |
| I = 127 | Sb = 120 | Te = 125 | Cs = 133 | Ba = 137 |

It will be seen that in each group the difference between the first and second number is about 16, while between all the others the increase in weight takes place by a number which approximates to 16 × 3.

These numerical relations between the atomic weights of elements of the same family, and between the various groups, is obviously not a chance one, and chemists were led by it to believe that the properties of the elements were in some way related to their atomic weights. Newlands (1864) was the first to point out, that if the elements are tabulated in the order of increasing atomic weights, the properties belonging to each of the first seven elements reappeared in the second seven, and he applied to this relation the name of *the law of octaves*. A more elaborated and systematic representation of Newlands' law of octaves was afterwards developed by Mendelejeff (1869), and which is now generally known as Mendelejeff's periodic law.

If the fourteen elements with lowest atomic weights, after hydrogen, be arranged in order of increasing atomic weights in two horizontal rows of seven, some of these relations will be recognised—

Li = 7 Be = 9 B = 11 C = 12 N = 14 O = 16 F = 19
Na = 23 Mg = 24 Al = 27 Si = 28 P = 31 S = 32 Cl = 35.5

In traversing the upper row from lithium to fluorine, we meet with certain characteristic properties belonging to each member, and also a certain gradation in those properties that are common. Coming to the second row, or octave, many of the characteristic properties of the members of the first row again appear, and the same regular modulation is met with in passing along the series: thus lithium resembles sodium, carbon corresponds to silicon, fluorine to chlorine, and so on. These resemblances are seen both in the physical as well as the chemical properties of the elements, thus lithium and sodium are both soft white metals, and are strongly electro-positive. Fluorine and chlorine are both pungent corrosive gases, and are intensely electro-negative. Taking their power of combining with chlorine and with hydrogen as indicative of their valency, we see that the change in this respect, as the two series are traversed, is the same in each, thus—

$$\begin{array}{llllllll}
LiCl & BeCl_2 & BCl_3 & \overbrace{CCl_4 \quad CH_4} & & NH_3 & OH_2 & FH \\
NaCl & MgCl_2 & (AlCl_3)_2 & SiCl_4 & SiH_4 & PH_3 & SH_2 & ClH
\end{array}$$

The gradation in properties exhibited by the elements in a series, is also seen in their power of combining with oxygen, which will be more clearly brought out if the formulæ of the compounds be so written as to indicate the relative proportions of oxygen with which two atoms of each element unites, thus—

$$\begin{array}{lllllll}
Na_2O & (Mg_2O_2) & Al_2O_3 & (Si_2O_4) & P_2O_5 & (S_2O_6) & Cl_2O_7{}^* \\
 & MgO & & SiO_2 & & SO_3 &
\end{array}$$

Regarding, then, the seven elements of the first row as a *period*, we find that the various properties exhibited by the several members are met with again in those of the second period.

Not only do the properties of the elements themselves reappear, but also those possessed by the various compounds they form; thus lithium chloride (LiCl) and sodium chloride (NaCl) strongly resemble one another. The oxides of beryllium and magnesium (BeO and MgO) have similar properties. The compounds of fluorine and chlorine with hydrogen (HF and HCl) closely resemble each other, and so on.

This periodic reappearance of similar properties, exhibited by the

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* Perchloric oxide is not known in the free state.

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elements and their compounds as the atomic weights of the former gradually increase, is thus stated by Mendelejeff in his law of periodicity. *The properties of the elements, as well as the properties of their compounds, form a periodic function of the atomic weights of the elements.*

When the tabulation of the elements according to this system is continued (after the completion of the second period with chlorine), it will be seen, that beginning with potassium, seventeen elements have to be arranged before we meet with the reappearance of those properties that belong to the first; that is to say, there are two sets of seven each, and three elements over, which in the following table are placed within brackets:—

| K. | Ca. | Sc. | Ti. | V. | Cr. | Mn. | (Fe. | Co. | Ni.) |
|---|---|---|---|---|---|---|---|---|---|
| 39 | 40 | 44 | 48 | 51 | 52 | 55 | (56 | 59 | 59) |

| Cu. | Zn. | Ga. | Ge. | As. | Se. | Br. |
|---|---|---|---|---|---|---|
| 63.5 | 65 | 70 | 72 | 75 | 79 | 80 |

This constitutes what is known as a *long period*, in contradistinction to the two first, which are distinguished as short periods. In certain respects, however, the last seven elements in this long period exhibit resemblances to the first seven; that is to say, the properties displayed by the members of the first period, which is known as the *typical period*, reappear twice over in the long period. The three elements within the brackets are termed by Mendelejeff *transitional elements*. Continuing the arrangement from bromine, another long period occurs, again containing three transitional elements:—

| Rb. | Sr. | Y. | Zr. | Nb. | Mo. | — | (Ru. | Rh. | Pd.) |
|---|---|---|---|---|---|---|---|---|---|
| 85.2 | 87.3 | 89.6 | 90.4 | 93.7 | 96 | ? | (103.5 | 104 | 106) |

| Ag. | Cd. | In. | Sn. | Sb. | Te. | I. |
|---|---|---|---|---|---|---|
| 108 | 112 | 113 | 118 | 120 | 125 | 127 |

It will be seen that a gap is left where the seventh member of the first part of this period should be, an element which would correspond, in this period, with manganese in the period above. This element is at present unknown. The remaining elements belong to three other long periods, in which, however, the number of gaps is very considerable, thus—

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Cs.<br>133 | Ba.<br>137 | La.<br>138.5 | Ce.<br>141 | — | — | — | (— | — | —) |
| | — | — | — | — | — | — | — | | |
| — | — | Yb.<br>173 | — | Ta.<br>182 | W.<br>184 | — | (Os.<br>(191 | Ir.<br>192.5 | Pt.)<br>195) |
| | Au.<br>197 | Hg.<br>200 | Tl.<br>203.7 | Pb.<br>207 | Bi.<br>207.5 | — | — | | |
| — | — | — | Th.<br>232 | — | Ur.<br>239.8 | — | (— | — | —) |
| | — | — | — | — | — | — | — | | |

Those elements that fall in the first seven places of the long periods, are termed the *even series*, while the last seven are distinguished as the *odd series;* arranging them, therefore, in such a manner as to bring the odd and even series into columns, we get the table on page 102.

In this manner the elements are arranged in eight groups, the eighth containing the transitional elements that come between the even and odd series of the long periods.

In each of the remaining seven groups, the elements belonging to the even series of their respective long periods, are placed to the left, while those belonging to the odd series are arranged on the right hand side of each vertical column. In this way the groups are divided into the subdivisions, A and B, in which the resemblance between the members is most pronounced. Thus in Group II., although there are certain properties common to all the members, there is a much closer similarity existing between the elements calcium, strontium, and barium than between zinc and calcium, or cadmium and barium.* The elements in the two short periods, have been placed in that subdivision or family, with the members of which they exhibit the closest resemblance. Thus, in Group I. lithium and sodium are more allied to potassium, rubidium, and caesium, than to copper, silver, and gold; while in Group VII.

---

* This, however, is by no means uniformly the case; thus the element copper (Group I.) in many of its chemical attributes is much more closely allied to mercury (Group II.) than to silver; and silver again more strongly resembles thallium (Group III.) than either copper or gold, with which it is associated in this system of classification.

| | Group I. | | Group II. | | Group III. | | Group IV. | | Group V. | | Group VI. | | Group VII. | | Group VIII. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | A | B | A | B | A | B | A | B | A | B | A | B | A | B | |
| 1st short, or typical, period | H<br>Li | | Be | — | — | B | — | C | — | N | — | O | — | F | |
| 2nd short period | Na | | Mg | | | Al | | Si | | P | | S | | Cl | |
| 1st long period, even series | K | | Ca | | Sc | | Ti | | V | | Cr | | Mn | | Fe, Co, Ni |
| 1st long period, odd ,, | | Cu | | Zn | | Ga | | Ge | | As | | Se | | Br | |
| 2nd long period, even series | Rb | | Sr | | Y | | Zr | | Nb | | Mo | | — | | Ru, Rh, Pd |
| 2nd long period, odd ,, | | Ag | | Cd | | In | | Sn | | Sb | | Te | | I | |
| 3rd long period, even series | Cs | | Ba | | La | | Ce | | — | | — | | — | | — — — |
| 3rd long period, odd ,, | | — | | — | | — | | — | | — | | — | | — | |
| 4th long period, even series | — | | — | | Yb | | — | | — | | W | | — | | Os, Ir, Pt |
| 4th long period, odd ,, | | Au | | Hg | | Tl | | Pb | | Bi | | — | | — | |
| 5th long period, even series | — | | — | | Th | | — | | — | | U | | — | | — — — |
| 5th long period, odd ,, | | — | | — | | — | | — | | — | | — | | — | |
| **Oxygen compounds** | $R_2O$ | | $R_2O_2$ | | $R_2O_3$ | | $R_2O_4$ | | $R_2O_5$ | | $R_2O_6$ | | $R_2O_7$ | | $(R_2O_8)$ |
| **Hydrogen compounds** | — | | — | | — | | $RH_4$ | | $RH_3$ | | $RH_2$ | | $RH$ | | |

fluorine and chlorine are placed in the same family with bromine and iodine, with which they exhibit a close similarity.

In the eighth group, containing the transitional elements, the families consist of the horizontal and not the vertical rows; that is to say, the closest resemblance is between the three transitional elements in each series, elements whose atomic weights, instead of exhibiting a regular increase, as in the other families, have almost the same value, such as Fe = 56; Co = 59; Ni = 59.

A glance at the table shows that in the last three long periods there are a large number of gaps. It is possible that these gaps may represent elements which yet await discovery. This supposition gains considerable support from the fact, that at the time Mendelejeff first formulated the periodic law, there were three such gaps in the first long period, which have since been filled up by the subsequent discovery of three new elements; these will be referred to later. It is noteworthy, however, that all the elements belonging to the last three periods, together make a total which is almost exactly the number required for a single complete long period, including three transitional elements; and it is quite possible that future investigations may necessitate an alteration in the accepted atomic weights of some of these elements, and consequently a change in their positions in the system.

The periodic recurrence of some of the chemical properties, is indicated in the lowest horizontal column, where the general formulæ of the oxygen compounds, and the hydrides, are given; R standing for one atom of any element in the group. As explained on page 99, these formulæ are so written as to show the relative amount of oxygen to two atoms of element, in order to establish the true relation between the different groups. For example, the oxides of the elements of Group I. contain two atoms of the element to one of oxygen, as $K_2O$; but those of the second group only contain one atom of the element, as CaO: hence the general formula is doubled, $R_2O_2$. It will be seen, therefore, that the proportion of oxygen relative to two atoms of the element regularly increases from the first group to the eighth. The oxides of the members of the first group are strongly basic in character, and in general this basic nature gradually diminishes as we traverse the series, giving place to acidic characteristics, which are strongly marked in the seventh group.

The periodic reappearance of the physical properties of the elements is seen in such points as their electrical characters, their malleability, ductility, melting-points, &c., all of which are in harmony with the periodic law; but in none is it more strikingly seen than in their atomic volumes in the solid state. The atomic volumes of the elements, are the relative volumes occupied by quantities proportional to their atomic weights, or by gramme-atoms; and they are obtained by dividing the atomic weights of the elements by their specific gravities. In the case of gases, as has been already explained on page 39, the specific gravity is the density referred to hydrogen as the unit: the atomic volume, therefore, of such a gas as oxygen is—

$$\frac{16 = \text{atomic weight}}{16 = \text{density}} = 1.$$

The specific gravities of solids (and also liquids) are referred to water as the unit, and as 1 cubic centimetre of water weighs 1 gramme, the specific gravity of a solid or liquid, expresses the weight in grammes of 1 cubic centimetre of the substance. Dividing the atomic weight, expressed in grammes, by the weight in grammes of 1 cubic centimetre (*i.e.*, the specific gravity), the atomic volume will be represented in cubic centimetres. It must be remembered that the atomic volumes do not express the relative volumes that are actually occupied by the atoms, they represent in reality the relative volume of the atoms *plus* the unknown volumes of the spaces that separate them.

The following table gives the specific gravities, and the calculated atomic volumes, of the first and the middle elements of the two short and two long periods.

| | | Specific Gravity. | Atomic Weights. | Atomic Volumes. |
|---|---|---|---|---|
| 1st Period | Lithium | 0.59 | 7 | 11.9 |
| | Carbon | 3.0 | 12 | 4 |
| 2nd Period | Sodium | 0.97 | 23 | 23.6 |
| | Silicon | 2.4 | 28.3 | 11.8 |
| 3rd Period | Potassium | 0.865 | 39 | 45 |
| | Iron (Cobalt-Nickel) | 7.79 | 56 | 7.2 |
| 4th Period | Rubidium | 1.52 | 85 | 56.0 |
| | (Ruthenium-Rhodium) Palladium | 11.4 | 106.2 | 9 |
| | Caesium | 1.88 | 133 | 70 |

From the figures in the last column it will be seen, that beginning with lithium, 11.9, the atomic volume falls as the middle element of the period, namely carbon, is reached; after which it again rises and reaches a maximum with the first member of the second period, namely sodium. In this period the same gradual fall in atomic volume is again noticed until the middle element (silicon) is reached, when the value of this function of the elements once more rises, and a second maximum is attained with the first member (potassium) of the third period. The two next are long periods, and the atomic volumes steadily decrease until the middle three (transitional) elements, after which they gradually increase again to a maximum in rubidium, the starting-point of the fourth period. In the fourth period the same thing once more occurs, the minimum atomic volumes being those of the middle or transition elements, after which a maximum is again reached in caesium.

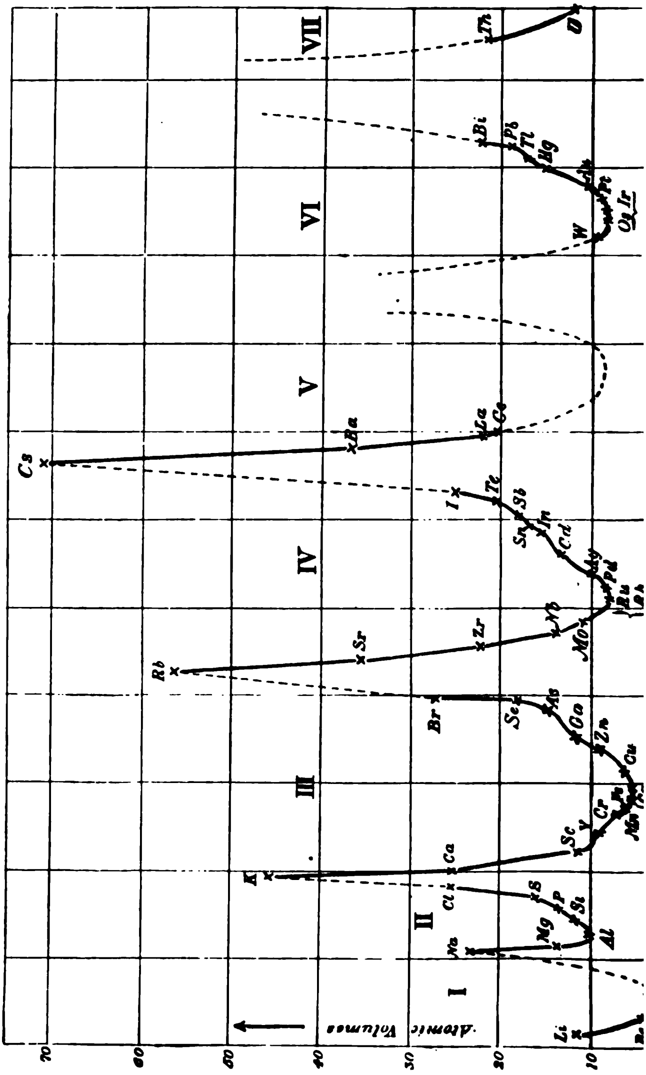
This periodicity of the atomic volumes may be graphically represented by a curve, where the ordinates represent atomic volumes, and the abscissæ atomic weights. This curve, which was first constructed by Lothar Meyer, is known as Lothar Meyer's curve (page 106), and a comparison of it with Mendelejeff's table is most instructive.

The divisions indicated by the Roman numerals correspond to the different periods: Groups I. and II. being the two short periods, III. and IV. the two complete long periods, while V., VI., and VII. correspond to the fragmentary portions of the last three periods.

The transitional elements of periods III., IV., and VI. are all to be found at the minima of the large hollows; separating the even series (situated on the descending portion of the curve), from the odd series which lie on the ascending slope. The elements belonging to the different groups in Mendelejeff's table, are seen to occupy the same relative positions upon the different portions of this curve.

Thus in Group I. the elements Li, Na, K, Rb, Cs, are all found upon the maxima of the curve, and Cu, Ag, and Au at those points at the minima where the electro-negative properties reappear. The halogen elements (chlorine, bromine, iodine) are seen in similar positions upon the ascending, and the alkaline earths (beryllium, magnesium, calcium, strontium, barium) on the descending portions.

When the periodic law was first formulated by Mendelejeff (1869), there were a number of instances in which the system did not harmonise with the then accepted atomic weights of the elements. The discoverer boldly asserted that the atomic weights,


Atomic Volumes
10
20
30
40
50
60
70
I
II
III
IV
V
VI
VII
Li
Na
Mg
Al
Si
P
S
Cl
K
Ca
Sc
V
Cr
Mn
Fe
Cu
Zn
Ga
As
Se
Br
Rb
Sr
Zr
Nb
Mo
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Cs
Ba
La
Ce
W
Os Ir
Pt
Au
Hg
Tl
Pb
Bi
Th
U

and not the system, were at fault, and in every such case the careful reinvestigation of the atomic weights by numerous chemists, has proved the correctness of the assertion. One or two instances may be quoted. The element indium had assigned to it the atomic weight 76. Its combining proportion is 38, and being regarded as a divalent element, its oxide was believed to have the formula InO. Having an atomic weight = 76, indium would occupy a place between As = 75 and Se = 79; but in the system (see table on page 102), there is no room for an element with such an atomic weight; and, moreover, if indium be a divalent element having this atomic weight, it should come between Zn = 65 and Sr = 87 in Group II., where again there is no room. Mendelejeff made the assumption that the oxide of indium had the formula $In_2O_3$, believing the element to be an analogue of aluminium (Group III.). If this be the true composition of the oxide, the atomic weight of the element would be 38 × 3 = 114, and indium would then take its place in Group III., between the elements cadmium = 112 and Sn = 118, in the odd series of the second long period. Bunsen afterwards determined the specific heat of indium by means of his ice calorimeter, and found it to be 0.057:—

$$\frac{\text{Mean atomic heat}\ \ 6.4}{\text{Specific heat}\ .\ .\ 0.057} = 112.3 = \text{atomic weight (see page 45).}$$

Hence 114 and not 76 is the accepted (approximate) atomic weight of indium.

Again, the element beryllium (formerly known as glucinum) has a combining proportion of 4.6. Its chloride was believed to have the composition $BeCl_3$, and its oxide to be a sesquioxide having the formula $Be_2O_3$. The atomic weight assigned to the element, therefore, was 13.8.

With this atomic weight beryllium would take its place between carbon = 12 and nitrogen = 14; but according to the periodic classification there is no room for such an element, and moreover, in such a position it would be among elements with which it has no properties in common. On the supposition that the oxide of beryllium has the formula BeO, that is, that the element is divalent, its atomic weight would have to be lowered from 13.8 to 9.1 in order to maintain the same ratio between the weights of metal and oxygen in the compound. On this assumption, beryllium would fall into the second place in the first series, between lithium = 7 and boron = 11, and in the same group as magnesium and zinc.

When the specific heat of beryllium was determined, it gave the value 0.45, and this number divided into the atomic heat constant, 6.4, gave 14 as the atomic weight. In spite of this evidence in favour of the higher value as the atomic weight of beryllium, Mendelejeff still regarded the lower number as correct, and it was suggested that possibly beryllium, like carbon and boron (elements also of very low atomic weight), had an abnormally low specific heat at ordinary temperatures. This was found to be the case (see page 46), and at 500° the specific heat of beryllium was found to be 0.6206. This divided into 6.4 gives the value 10 as the atomic weight, which indicates that 9.1 and not 13.8 is in reality the atomic weight of beryllium.

Not only has the periodic law been of service in bringing about the correction of a number of doubtful atomic weights, but by means of it, its originator was enabled to predict with considerable certainty the existence of hitherto undiscovered elements, and even to predicate many of the properties of these elements. As already mentioned, at the time when the periodic law was first formulated, there were three gaps in the system in the first long period, namely, No. 3 in the even series (now occupied by scandium), and Nos. 3 and 4 in the odd series (now filled by gallium and germanium). To the unknown elements which were destined to occupy these positions, Mendelejeff gave the names *eka-boron*, *eka-aluminium*, and *eka-silicon* (the prefix eka being the Sanscrit numeral *one*), and from the known properties of the neighbouring elements of the series (horizontal rows in the table, page 102), and also of those situated nearest in the same family (vertical columns), he predicted some of the prominent properties that would probably be possessed by these elements. Thus in the case of eka-aluminium, from the known properties of aluminium and indium, the neighbouring elements in the same family, and from zinc, the contiguous element in the same series (the 5th place in the series being unoccupied), Mendelejeff deduced the following properties for the unknown element that he called eka-aluminium :—

### PREDICTED PROPERTIES OF EKA-ALUMINIUM (1871).

(1.) Should have an atomic weight about 69.
(2.) Will have a low melting-point.
(3.) Its specific gravity should be about 5.9.
(4.) Will not be acted upon by the air.

(5.) Will decompose water at a red heat.
(6.) Will give an oxide $El_2O_3$, a chloride $El_2Cl_6$, and sulphate
$_2(SO_4)_3$.
(7.) Will form a potassium alum, which will probably be more
able and less easily crystallisable than the corresponding alumi-
m alum.
(8.) The oxide should be more easily reducible to the metal than
mina. The metal will probably be more volatile than alumi-
m, and therefore its discovery by means of the spectroscope
y be expected.

n the year 1875 Lecoq de Boisbaudran discovered a new
nent in a certain specimen of zinc blende (zinc sulphide), the
ividuality of which he first recognised by the spectroscope,
spectrum being characterised by a brilliant violet line. This
nent he named *gallium*. The properties of this metal, as they
e subsequently observed, showed that it was, in fact, the pre-
ed eka-aluminium of Mendelejeff, as will at once be seen by a
parison of the following facts.

PROPERTIES OF GALLIUM (*discovered* 1875).

1.) Atomic weight = 69.9.
2.) Melting-point, 30.15°.
3.) Specific gravity, 5.93.
4.) Only slightly oxidised at a red heat.
5.) Decomposes water at high temperatures.
6.) Gallium oxide, $Ga_2O_3$. Gallium chloride, $Ga_2Cl_6$. Gallium
phate, $Ga_2(SO_4)_3$.
7.) Forms a well-defined alum.
(8.) Is easily obtained by the electrolysis of alkaline solutions.

In a similar manner the properties of *eka-boron* and *eka-silicon*
re predicted, and the subsequent discovery of *scandium* (Nilson,
79), and *germanium* (Winkler, 1886), whose properties were
und to closely accord with these hypothetical elements, formed
additional demonstration of the truth of the periodic law.

No satisfactory theory has yet been offered, to explain the law of
eriodicity.

# CHAPTER XIII

## *GENERAL PROPERTIES OF LIQUIDS*

UNDER this head the following subjects will be considered:—

1. The passage of liquids into vapours or gases.
2. The passage of liquids into solids.
3. Solution.

**1. The Passage of Liquids into Gases. Evaporation and Boiling.**—Just as in the gaseous condition, so in the liquid state, the molecules are in a state of motion: in the liquid state, however, the mean kinetic energy of the molecules is unable to overcome the force of their mutual attraction. Some of the molecules have a smaller kinetic energy (that is, a lower temperature), and others a greater kinetic energy, than the average; and when in the course of their movements the latter strike the surface of the liquid and break through it, they continue their movements in the space above, as gaseous molecules. If the space into which they wander be unlimited, that is, if the liquid be freely exposed to the air, these molecules escape away altogether, and consequently the liquid diminishes in quantity. This process is known as *evaporation*, and as the molecules which so leave the liquid are those having the highest temperature, it follows that the temperature of the liquid, which is the average temperature of the molecules, will fall. The more completely the molecules that so escape from the surface of a liquid are prevented from falling back, that is, the more rapidly they are swept away from the immediate neighbourhood of the liquid, the more quickly will this escape of molecules take place, and therefore the greater will be the fall of temperature that results from evaporation. Thus, if a quantity of liquid, say water, be exposed in a dish so that a current of air is blown across the surface, the rate of evaporation is increased, and the temperature consequently falls lower than if the water be merely placed in a still atmosphere: similarly, if the water be placed in a vacuum the rate of evaporation is increased, because the molecules that escape from the surface of the liquid are not impeded in their motions by collisions with the molecules of air.

This fall of temperature resulting from evaporation, may be readily seen by enveloping the bulb of a thermometer in a piece of thin muslin, and moistening it with water. If such a thermometer be placed by the side of a naked thermometer, it will be seen that the mercury will fall lower in the one that is moistened, and the difference will be still more marked if the instruments are placed in a draught, whereby the evaporation of the water from the muslin is accelerated.

If the space above the liquid be limited, molecules still continue to escape from the surface; but a state of equilibrium is soon established, when as many are thrown back again by rebounding from one another and from the walls of the containing vessel, as leave the surface in a given time. Under these conditions the enclosed space is said to be *saturated with the vapour of the liquid.* The number of molecules which escape from the surface, depends upon the temperature, and s independent of the pressure, for if the volume of a saturated vapour be forcibly diminished, t merely results in the condensation of a portion of the vapour; and f expanded, a corresponding vaporisation of an additional quantity of the liquid, the pressure remaining always constant. The number of molecules that re-enter the liquid, is determined by the number and the velocity of those that exist as gaseous molecules in a unit volume. But the pressure exerted by a gas is caused by the number and velocity of the molecules in a given volume, hence the

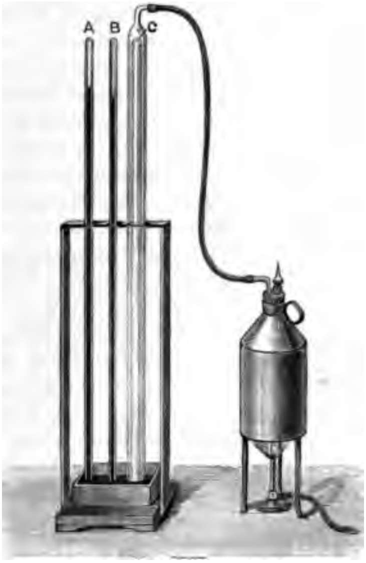


FIG. 12.

condition of equilibrium is set up, when the vapour above the liquid exerts a definite pressure, which pressure will be constant for any given temperature. The pressure exerted by a vapour under these conditions is termed the *vapour tension* of the liquid. The fact that the vapour given off from a liquid exerts pressure, may readily be experimentally illustrated by means of the apparatus seen in Fig. 12. Three glass tubes, A, B, and C, about one metre long, are completely filled with mercury and inverted in a trough of the same liquid. The mercury will sink to the same level in each tube, the length of the mercury column representing the atmospheric pressure at the time. Into two of these barometer tubes, B and C, a few drops of water are introduced, when it will be found that the mercury is depressed, as indicated in B, below the level at which it previously stood. This depression of the mercury column, represents the tension of the vapour of the water for the particular temperature at which the experiment is made. If tube C be surrounded by a wider glass tube, through which steam from a small boiler is passed, it will be noticed that as the temperature of the water in the tube rises, the mercury is more and more depressed, thus showing that the tension of the vapour increases with rise of temperature. As soon as the steam circulates freely and is escaping at the bottom of the wide tube, in other words, as soon as the temperature of the enclosed water in tube C reaches 100°, *i.e.*, the temperature of the steam surrounding it, the mercury in the tube will be depressed to the level of that in the trough. The tension of the vapour within the tube, under these circumstances, is therefore equal to the atmospheric pressure.

If, instead of introducing water into the barometer tube, ether were employed, and a stream of vapour from boiling ether were passed through the outer tube, it would be seen that when the ether within the tube reached the temperature of the vapour from the boiling ether, namely, 35°, the mercury would again be depressed to the level of that in the trough; that is, the tension of the ether vapour would then be equal to the pressure of the atmosphere. We see, therefore, that when water is heated to its boiling-point, viz., 100°, the tension of its vapour is equal to the atmospheric pressure; and when ether is heated to *its* boiling-point, viz., 35°, the pressure exerted by *its* vapour is equal to the pressure of the atmosphere. The boiling-point of a liquid may therefore be defined as *the temperature at which the vapour pressure is equal to the pressure of the atmosphere.* As soon as this point is passed, the kinetic energy of the molecules has been so much augmented by the supply of external heat, that it is able to overcome the force of their mutual attractions, and, consequently, the molecules freely pass away from the surface of the liquid.

As will be seen from the illustrations given, namely, water and ether, the temperatures at which the vapours of different liquids exert a pressure equal to that of the atmosphere are widely different. This fact will be still more evident from the following table, giving the temperatures at which the vapour pressure of various liquids is equal to the standard atmospheric pressure :—

| | |
|---|---|
| Liquid oxygen . . . . . | − 181° |
| Liquid nitrous oxide . . . . | − 92° |
| Liquid sulphur dioxide . . . | − 10° |
| Ethyl chloride . . . . . | + 11° |
| Carbon disulphide . . . . | 47° |
| Water . . . . . . . | 100° |
| Aniline . . . . . . . | 182° |
| Mercury . . . . . . . | 358° |

Since the boiling-point of a liquid is that temperature at which its vapour tension is equal to the atmospheric pressure, it will be evident that, if the latter increases or decreases, the temperature necessary to produce an equal vapour pressure must also rise or fall; in other words, the boiling-point of a liquid is dependent upon the pressure. If a quantity of water, no warmer than the hand, be placed beneath the receiver of an air-pump, which is then quickly exhausted, the water will be seen to enter into violent ebullition. It does this, when the pressure within the receiver is reduced to the point at which it is equal to the tension of aqueous vapour at the temperature taken.

For this reason water boils at a lower temperature in high altitudes than at the sea-level; and as the vapour tension of water at various temperatures has been experimentally determined, we can, by ascertaining the boiling-point of water at any particular altitude, calculate the atmospheric pressure, and consequently the height above the sea-level.

Many liquids when heated, especially in glass vessels that have been carefully cleansed, may be raised several degrees above the boiling-point without ebullition taking place. The liquid under these circumstances assumes a pulsating movement, which continues for a short time, when a burst of vapour is suddenly evolved with violence, and the temperature at once drops to the boiling-point. The liquid then becomes quiescent, and again, as the temperature rises, the pulsating movement begins, ending once more in an explosive evolution of vapour. This successive boiling, or *bumping*, is sometimes sufficiently violent to cause the fracture of the vessel. In order to experimentally ascertain the boiling-point of a liquid, the thermometer, for this reason, is not immersed in the *liquid*, but is suspended in the vapour, the temperature of which remains constant throughout these irregularities in the boiling.

**Latent Heat of Vaporisation.**—When a liquid is heated, its temperature rises, as indicated by the thermometer, until a certain point is reached (the boiling-point of the liquid), when the continued application of heat causes no further rise of temperature. Thermometers placed in the liquid, and in the vapour, indicate the same temperature and remain constant, and all further application of heat is unappreciated by these instruments, and disappears in changing the liquid into vapour. The heat which in this way is absorbed during the vaporisation of a liquid, is spoken of as the *latent heat of vaporisation;* and the same amount of heat which thus disappears during the conversion of a liquid into a vapour, is again rendered sensible when the vapour passes back into the liquid state.

The heat which is thus said to become *latent*, is in reality converted into kinetic energy; it is expended in imparting to the molecules the kinetic energy necessary to overcome the attractive forces operating between them while in the liquid state; in other words, it is doing the work of overcoming cohesion (internal work), and also the external pressure on the vapour (external work).

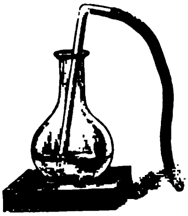


FIG. 13.

In order that a liquid may pass into a vapour it is necessary that heat be absorbed. We have seen (page 110) that a liquid undergoing spontaneous evaporation becomes colder (that is, heat is absorbed by the molecules that are converted into the gaseous state), and also that the more rapidly the liquid can be made to pass into the vaporous condition, without supplying external heat, the lower will its temperature fall. Upon this fact depend a number of methods for the artificial production of low degrees of cold. For example, ether boils at 35°, but if a small quantity of ether be placed in a glass flask standing upon a wooden block, upon which a few drops of water have been poured, and a current of air from a bellows be briskly blown through the ether (Fig. 13), the temperature of the ether will fall so rapidly that in a few moments the flask will be frozen to the block. By the rapid evaporation of liquids with lower boiling-points, the extreme degrees of cold necessary for the liquefaction of such gases as oxygen, carbon monoxide, air, &c., are obtained. Thus, liquid methyl chloride boils at −23°; by causing it to rapidly vaporise, its temperature can be reduced to −70°. Liquid ethylene in the same way falls to a temperature of −120°, and liquid oxygen by rapid evaporation gives a temperature as low as −210°.

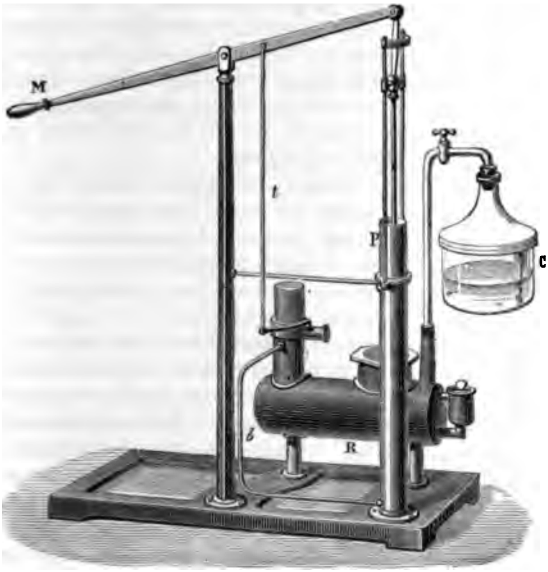


FIG. 14.

The temperature of water, in like manner, may be so lowered by its own rapid evaporation, as to cause it to freeze. We have already seen that by reducing the pressure, the boiling-point of a liquid is lowered; if, therefore, a quantity of water be placed in a vacuum, and methods be adopted to remove the water vapour as rapidly as it is formed, the water will enter into rapid ebullition. The evaporation will therefore proceed so rapidly, and consequently absorb heat so quickly, that the temperature of the boiling liquid will quickly fall to 0° when it passes into the solid state. The instrument known as Carré's freezing machine depends upon this principle. The water to be frozen is placed in the glass bottle C (Fig. 14), which is in connection with a metal reservoir R, half filled with strong sulphuric acid. This in its turn is connected by *b* with an air-pump P, worked by the lever M, to which is also attached a connecting rod *t*, so that a stirrer within the reservoir is kept constantly in motion. As soon as the apparatus is exhausted to a pressure of two or three millimetres, the water begins rapidly to boil, and as the sulphuric acid absorbs the water vapour as rapidly as it is given off, the temperature quickly falls and the water freezes.

Fig. 15 illustrates another method by which the same result may be obtained. A tall glass vessel is exhausted by means of an ordinary air-pump, and water is allowed slowly to enter from a stoppered funnel, upon the end of which is secured a short string. At the same time strong sulphuric acid is admitted by the second funnel, and caused to flow down a glass rod, round which is wound a spiral of asbestos thread. The acid at once absorbs the aqueous vapour from the evaporating water, the temperature of which, therefore, falls below the freezing-point, and it solidifies as it flows over the string into the form of an icicle.

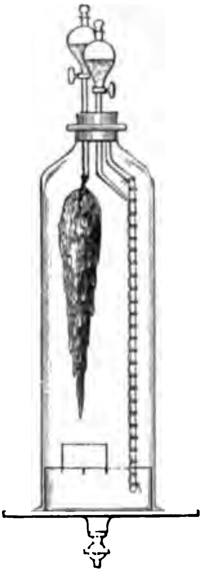


Fig. 15.

Just as diminution in pressure lowers the boiling-point of a liquid, so increased pressure raises the boiling-point. If water be heated in a closed iron vessel, as in a high-pressure steam boiler, the pressure caused by its own vapour raises the boiling-point many degrees above 100°. There is a definite temperature, however, for every liquid, beyond which the liquid state is impossible, whatever may be the pressure; that is to say, the liquid when heated beyond this fixed point passes into the gaseous state, however great the pressure may be. This temperature is the *critical*

*\'perature* (see page 77). If a liquid be heated in a sealed and ong glass tube, as the critical temperature is approached, the face of the liquid gradually becomes ill-defined, and finally the e is completely occupied by transparent vapour. On again oling, as soon as the critical point is passed, the contents of : tube again separate into two distinct layers consisting of liquid d gas.

**Vapour-Pressures of Solutions.**—The boiling-point of a liquid modified by the presence in the liquid of dissolved substances. the substance in the solution be less volatile than the liquid, the iling-point is raised. Thus, while the boiling-point of pure ter (under the normal atmospheric pressure) is 100°, the tem-rature at which saturated aqueous solutions of salts boil, is nsiderably higher, thus :—

| Water Saturated with | Containing Grammes of Salt in 100 Grammes of Water. | Boiling-point. |
|---|---|---|
| Sodium chloride . . . | 41.2 | 108.4° |
| Potassium nitrate. . . | 335.1 | 115.9° |
| Potassium carbonate . . | 205.0 | 133.0° |
| Calcium chloride . . . | 325.0 | 179.5° |

The temperature of the steam of these boiling solutions, as certained by suspending a thermometer in the vapour, appears be the same as that from pure water, as the thermometer in cases indicates 100°. In reality, however, the temperature is gher, although not so high as that of the boiling liquid. The ason that the thermometer indicates 100° in all cases is because : water vapour continually condenses upon the bulb of the strument, covering it with a film of pure water, which boiling from the bulb indicates only the boiling-point of the pure uid. By special arrangements this condensation may be pre-nted, when it has been shown (Magnus) that the temperature the vapour, from such boiling solutions, rises as the solutions come more concentrated—that is, as the temperature of the iling liquids rise. It has been already explained that the boil-g-point of a liquid is that temperature at which the vapour nsion is equal to the atmospheric pressure ; since, then, the esence of dissolved substances raises the boiling-point, it erefore lowers the vapour-pressure, for (in the case of aqueous utions) when the temperature has reached 100° the vapour-pressure is still below that of the atmosphere, for the liquid does not enter into ebullition at that temperature. By measuring vapour-pressures of solutions at a constant temperature, instead of measuring the temperature at a constant pressure (*i.e.*, the boiling-point), the following general laws have been established:—

1. *The relation between the quantity of a substance in solution and the diminution of the vapour-pressure below that of the pure solvent, is the same at all temperatures.*

2. *The diminution of the vapour-pressure of a liquid, by a dissolved substance, is proportional to the amount of the substance in solution (provided the substance itself exerts no appreciable vapour-pressure at the temperature of the experiment).*

3. *The molecular lowering of vapour-pressure by chemically similar substances is constant; that is to say, solutions containing one molecular weight in grammes (one gramme-molecule) of such substances in equal volumes of the solvent, give rise to the same diminution of vapour-pressure.*

4. *The relative lowering of vapour-pressure is proportional to the ratio of the number of molecules of the dissolved substance, to the total number of molecules in the solution, i.e., the sum of the number of molecules of the dissolved substance and of the solvent.**

Upon these considerations it becomes possible, by means of the lowering of the vapour-pressure, to find the molecular weight of a substance that is capable of being dissolved in a volatile liquid.

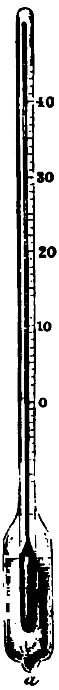


FIG. 16.

**The Passage of Liquids into Solids.**—Most liquids, when cooled to some specific temperature, pass into the solid state; the temperature at which this change takes place is termed the solidifying point. Generally speaking, the temperature at which a liquid solidifies is the same as that at which the solid again melts; but as the solidification of a liquid is subject to disturbances from causes that do not affect the melting-point, this is not always the case. Thus, water may be cooled many degrees below 0° if it be previously freed from dissolved air, and be kept perfectly still. This supercooling of water may readily be illustrated by means of the apparatus represented in Fig. 16. This consists of a thermometer whose bulb is enclosed in a larger bulb containing water, which before the bulb is sealed at *a*, is briskly boiled to expel all the air. When the instrument is immersed in a freezing mixture the temperature of the water may be lowered to − 15° without congealation taking place, but on the slightest agitation it at once solidifies and the temperature rises to 0°. It is on account of this property of water to suspend its solidification, that in determining the lower fixed point of a thermometer, the temperature of melting ice, and not that of freezing water, is made use of.

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* Except in the case of electrolytes. See page 96.

Many other liquids exhibit suspended solidification to a very high degree; thus glycerine may be cooled to − 30° or − 40° without solidifying, but if a crystal of solid glycerine be placed in the liquid the entire mass freezes, and does not again melt until a temperature of 15.5° is reached.

**Change of Volume on Solidification.**—Most liquids, in the act of solidifying, contract; that is to say, the solid occupies a smaller volume than the liquid. Consequently the solid is specifically denser, and sinks in the liquid. Thus 100 volumes of liquid phosphorus at 44° (the melting-point) when solidified, occupy only 96.7 volumes. Water expands upon solidification, hence ice is relatively lighter than water, and floats upon the liquid. The reverse change of volume accompanies the change of state in the opposite direction.

**Effect of Pressure upon the Solidifying Point of Liquids.**—In the case of liquids that contract upon solidification, increased pressure raises the point of solidification, and consequently raises the melting-point of the solid. The effect, however, is extremely small: thus the solidifying point (and melting-point) of spermaceti under the standard atmospheric pressure is 47.7°, while under a pressure of 156 atmospheres it is raised to 50.9°.

With liquids that expand on solidification, increased pressure has the opposite effect, and lowers the solidifying point. Thus, water under great pressure may be cooled below 0° and still remain liquid; and in the same way, ice may be liquefied by increased pressure without altering its temperature. In the case of water it has been found that an increased pressure of $n$ atmospheres, lowers the solidifying point by $0.0074n^\circ$; hence under a pressure of 135 atmospheres, the freezing-point of water (and the melting-point of ice) is lowered 1°. This lowering of the melting-point of ice under pressure may be illustrated by the experiment represented in Fig. 17. Over a block of ice is slung a fine steel wire, to which are hung a number of weights. The pressure thus exerted upon the ice, by lowering the melting-point, causes the ice to liquefy immediately beneath the wire, which therefore gradually cuts its way through the block. But as the wire passes through the mass, each layer of water behind it, again resolidifies, being no longer subject to the increased pressure; hence, although the wire cuts its way completely through the ice, the block still remains intact.

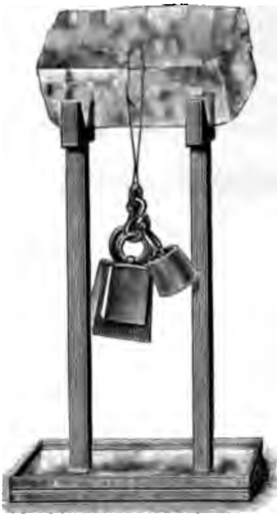

Fig. 17.

**Latent Heat of Fusion.**—When a liquid, at a temperature above its solidifying point, is cooled, a thermometer placed in the liquid indicates its loss of heat until solidification begins. At this point the temperature remains constant until solidification is complete, when the thermometer again begins to fall. And again, when a solid, at a temperature below its melting-point, is heated, its temperature rises until the melting begins, but no further rise of temperature takes place by the application of heat, until liquefaction is complete. The sensible heat that so disappears during fusion is spoken of as the *latent heat of fusion.* Just as in the passage of liquids into gases, this so-called latent heat represents heat that has ceased to be *heat*, but which is converted into kinetic energy that is taken up by the molecules: when the liquid passes back into the solid state, this energy is again transformed into sensible heat.

The fact that heat is thus changed into energy, and so rendered insensible to the thermometer, may be seen by adding boiling water to powdered ice. A thermometer placed in ice indicates the temperature 0°, and although boiling water is poured upon it, so long as any ice remains unmelted no rise of temperature of the mixture results, the heat contained in the boiling water being expended in doing the work of liquefying the ice, and converting it into water at 0°. When such an experiment is made more exactly, it is found that 1 kilogramme of water at 80.25°, when mixed with 1 kilogramme of ice at 0°, gives 2 kilogrammes of water at 0°. That is to say, the amount of heat contained in a kilogramme of water at 80.25°, is exactly capable of transforming an equal weight of ice at 0° into water at 0°.

As the heat required to raise the temperature of 1 kilogramme of water from 0° to 1° is the unit of heat, or *major calorie*, we say that the latent heat of fusion of ice is 80.25 thermal units, or calories.

During the solidification of a liquid, the latent heat of fusion is again given out. The solidification, therefore, only takes place gradually, for the heat evolved by the congelation of one portion, is taken up by the neighbouring particles, whose solidification is thereby retarded until this heat is dissipated. In the case of super-cooled liquids and super-saturated saline solutions, the solidification takes place more suddenly, and the evolution of the latent heat is therefore manifest by a rise of temperature.

**Effect of Substances in Solution upon the Solidifying Point of a Liquid.**—It has long been known, that a lower degree of cold is necessary to freeze salt water than fresh ; and also that the water obtained by remelting ice from frozen sea water, is so little salt as to be drinkable. Careful experiments have shown that when an aqueous solution of a salt is frozen, pure ice alone separates out, provided the solution is sufficiently dilute to prevent the dissolved salt from crystallising out on account of the reduction in temperature. This also holds in the case of all other solvents that are capable of being solidified, the pure solidified solvent alone separating when the solution is frozen. The effect of dissolved substances in lowering the solidifying point of the solvent was first discovered by Blagden (1788), who formulated the law that the depression of the freezing-point of aqueous solutions of the same substance, was proportional to the strength of the solution. By referring the lowering of the solidifying point to quantities of the dissolved substances that were in molecular proportions, instead of to equal weights, modern physicists have established the following general law : *Solutions containing in equal volumes of the solvent, quantities of dissolved substances proportional to their molecular weights, have the same point of solidification.**

The relations thus established between the molecular weight of a compound and its influence in lowering the solidifying point of a solvent, furnishes a method for the determination of the molecular weight of a substance.

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* Except in the case of electrolytes. See page 96.

# CHAPTER XIV

## *SOLUTION*

A SOLUTION may be defined as a homogeneous mixture of eit gas, a liquid, or a solid, with a liquid, this liquid being terme *solvent.**

Substances that are capable of forming such homogeneous tures with a solvent, are said to be soluble in that liquid. solution of matter in its three states will be treated separately.

1. **Solution of Gases in Liquids.**—When a gas is diss by a liquid, the liquid is said to *absorb* the gas, and althougl held that most liquids are capable of absorbing most gases greater or less degree, most of the investigations in this dire have been made with the two liquids, water and alcohol, by Bu

The quantity of a gas which a liquid is capable of abso depends upon four factors—(1) the specific nature of the li (2) the nature of the gas; (3) the temperature of the liquid the pressure.

(1.) The influence of the solvent may be seen by a comparis the quantities of the same gas which equal volumes of water of alcohol are capable of dissolving, thus—

100 volumes of water at 0° dissolve 179.6 volumes of carbon diox
while 100 ,, alcohol ,, 432.9 ,, ,,

(2.) The various quantities of different gases which the liquid will absorb are found to extend over a very wide r thus—

100 volumes of water at 0° dissolve 4.114 volumes of oxyg
while 100 ,, ,, ,, 114800.0 ,, ammo

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* Mixtures of gases are sometimes regarded as solutions, one gas bein to be dissolved in the other. Gases also are sometimes spoken of as diss liquids and solids, when liquid and solid substances directly vaporis them.

(3.) The volume of any gas which a liquid can absorb, diminishes with rise of temperature. This will be seen from the following table, where the volumes of different gases are given which 100 volumes of water will absorb at various temperatures.

| Temperature. | Carbon Dioxide. | Nitrous Oxide. | Oxygen. | Nitrogen. |
|---|---|---|---|---|
| 0 | 179.6 | 130.5 | 4.11 | 2.03 |
| 5 | 144.9 | 109.3 | 3.62 | 1.79 |
| 10 | 118.4 | 91.9 | 3.25 | 1.60 |
| 20 | 90.1 | 67.0 | 2.83 | 1.40 |

It was at one time believed that the solvent power of water for hydrogen was the same at all temperatures between 0° and 25°. Recent experiments have shown, however, that there is no exception to the general law in this case; thus it has been found that 100 volumes of water—

At 0° dissolve 2.15 volumes of hydrogen.
At 5° „ 2.06 „ „
At 10° „ 1.98 „ „
At 20° „ 1.84 „ „

When a solution of a gas in water is heated, the gas being less soluble at the higher temperature is expelled, and in most cases the whole of the gas is driven off at the boiling temperature. This, however, is not invariably the case; for example, the solution of hydrochloric acid in water, when boiled, will distil, without further evolution of gas, when a solution of definite strength is reached (see Hydrochloric Acid).

(4.) The influence of pressure upon the volume of a given gas which a liquid can absorb, was discovered by Henry (1803), and is known as Henry's law, namely, *The volume of the gas absorbed by a liquid is directly proportional to the pressure of the gas.* If the pressure be doubled, the same volume of liquid will dissolve twice the volume of the gas, the volume in each case being measured at 0° and 760 mm. But since, according to Boyle's law, the volume of a gas is inversely as the pressure, this law may be thus stated: *A given volume of a liquid will absorb the same volume of a gas at all pressures.*

Thus, if 100 volumes of water at 0° dissolve 2.03 volumes of nitrogen, under the standard atmospheric pressure (the volume of the gas being measured at 0° and 760 mm.), under twice this pressure, *i.e.*, two atmospheres, the same volume will absorb twice the volume of nitrogen, viz., 4.06 volumes *measured at* 0° *and* 760 *mm.* But 4.06 volumes of gas measured at 0° and 760 mm. occupy 2.03 volumes under a pressure of two atmospheres, therefore the liquid dissolves the same volume of compressed gas as of gas under ordinary pressure.

Henry's law is sometimes stated in a slightly altered form. If the quantity of gas present in a unit volume of both the liquid and the space above it, be called the *concentration* of the gas, then the law may be expressed by saying that *under all pressures, the ratio of the concentrations of the gas in the liquid, and in the space above it, remains constant.* This ratio is termed the *coefficient of solubility*, or the "solubility" of the gas in the particular liquid.

The term *coefficient of absorption*, first introduced by Bunsen, is the volume of the gas measured at 0° and 760 mm., which is absorbed by 1 cubic centimetre of a liquid at the same temperature and pressure ; and it is therefore simply the volume representing the "solubility" of the gas, reduced to 0°.

The solubility of gases in liquids is measured by agitating a known volume of liquid with a measured volume of the gas, under determinate conditions of temperature and pressure. The apparatus employed by Bunsen, and known as Bunsen's absorptiometer, is shown in Fig. 18. It consists of a graduated tube *e*, into which known volumes of the gas and liquid are introduced. The lower end of this tube is furnished with an iron screw, by means of which it can be securely screwed down upon an indiarubber pad, in order to completely close the tube (seen in the side figure). The tube containing the gas and liquid under examination, is lowered into a tall cylinder *g g*, in the bottom of which is a quantity of mercury. The cylinder is then filled with water, and the cap *p* screwed down. The thermometer *k* registers the temperature. The apparatus is then briskly shaken, in order that the liquid in the eudiometer may exert its full solvent action upon the gas, and on slightly unscrewing the tube from the caoutchouc pad mercury enters to take the place of the dissolved gas. The tube is again closed and the shaking repeated, and these operations are continued until no further absorption results. Finally, the volume of gas is measured, the temperature noted, and the pressure

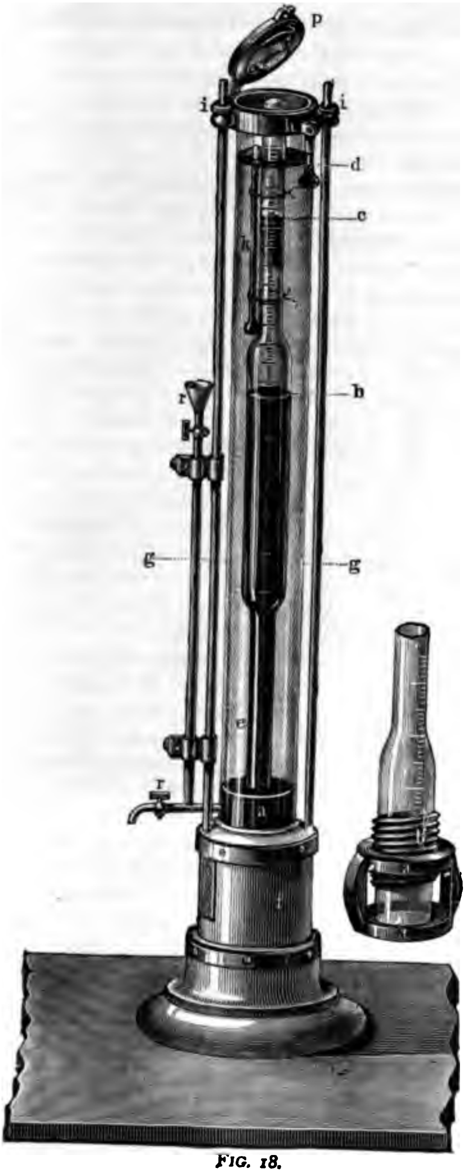

FIG. 18.

ascertained by reading the position of the mercury within the tube, and deducting the height of the column from *b* to the surface of the mercury a, from the barometric pressure at the time of making the experiment. The temperature of the water in the cylinder may be varied, and the coefficient of absorption at different temperatures can thus be determined.

Fig. 19 represents a more modern absorptiometer, being a modified form of Heidenhain and Meyer's apparatus. In this instrument the measuring tube and the absorption vessel are separate, and it admits of the use of much larger volumes of liquid. By means of the three-way cock *a*, the gas to be experimented upon is introduced into *A* by first raising and then lowering *B*; and the volume is measured when the levels of the mercury in *A* and *B* are coincident. By means of the three-way cock *b*, the vessel *C*, of known capacity, and which is connected with *A* by means of a flexible metal capillary tube, is filled with the desired liquid. The vessels *A* and *C* are then put into communication, and by raising *B* and opening the tap *c*, a definite volume of the liquid is run out into a measuring vessel, which represents the volume of gas that enters. The gas and liquid are then thoroughly agitated, after which the gas is passed back into *A* by lowering *B*, and, when *A* and *C* are in communication, opening the tap *c* beneath mercury. By measuring the diminution in volume suffered by the gas, the volume absorbed by the known volume of liquid is obtained. The measuring tube and absorption vessel are kept constant at any desired temperature, by surrounding them by water, or with vapours at known temperatures.

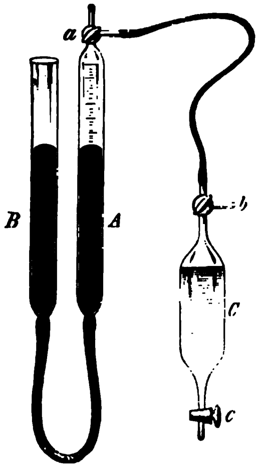

FIG. 19.

**Solubility of Mixed Gases.**—When two gases are mixed together, the pressure exerted by each is the same as would be exerted if the other were absent, and the entire space were occupied by the same mass of the one. Thus, if a mixture of two gases are in the proportion of two volumes of one and one volume of the other, the pressure exerted by the one present in larger proportion will be twice as great as that of the other; this pressure is termed the *partial pressure* of the gas under the circumstances, and obviously the total pressure of the mixture will be the sum of the partial pressures of the constituents. As the solubility of a gas in a liquid is proportional to the pressure, the solubility of the gases in a gaseous mixture will be influenced by the proportions in which they are present in the mixture. This is known as Dalton's law of partial pressures, which may be thus stated: *The solubility of a gas in a gaseous mixture is proportional to its partial pressure.* For example, the atmosphere consists of a mixture of oxygen and nitrogen, in the proportion of four volumes of nitrogen to one volume of oxygen (in round numbers). The partial pressure exerted by the oxygen is therefore only one-fifth of the total atmospheric pressure, and consequently the amount of oxygen which a given volume of a liquid is capable of dissolving from the atmosphere, is only about one-fifth of that which it will absorb from pure oxygen—in other words, will be one-fifth the absorption coefficient of oxygen for that liquid.

The application of the law of partial pressures will be seen in the solvent action of water upon the atmosphere. Taking the coefficients of absorption of oxygen and nitrogen for water as given by Bunsen—

$$\text{Oxygen} = .04114\,; \qquad \text{Nitrogen} = .02035,$$

and the proportion of oxygen to nitrogen in the air as one to four, by volume, we get—

$$\frac{.04114}{5} = .00823, \text{ and } \frac{.02035 \times 4}{5} = .01628,$$

or the number of cubic centimetres of oxygen and nitrogen which will be dissolved from the atmosphere, by 1 cubic centimetre of water at 0°.

One hundred volumes of water, therefore, will dissolve 2.451 volumes of air, of which .823 volumes is oxygen and 1.628 volumes of nitrogen; and if this dissolved air be again expelled from the water, by boiling, the air so obtained will contain oxygen and nitrogen in the proportions—

| | |
|---|---|
| Oxygen . . . . . . | 33.6 |
| Nitrogen . . . . . . | 66.4 |
| | 100.0 |

If a mixture of oxygen and nitrogen in this proportion be more dissolved in water, since the percentage of oxygen has from 20 to 33.6, and the partial pressure proportionately incre the mixture of the two gases that will be dissolved, will be richer in oxygen ; and after solution in water for the third tim boiled-out air will be found to contain as much as 75 per of oxygen. It will be obvious that the partial pressure which termines the extent to which the separate gases in a mixture dissolved, is not represented by the proportion in which the g are present *before* solution, but that in which they exist in gaseous mixture *after* the solvent has become saturated.

Henry's law does not hold good in the case of such very sol gases as ammonia, hydrochloric acid, &c. These gases appe enter into a true chemical union with the water, and in mo these cases, the act of solution is attended with considerable e tion of heat. In some of these instances the deviation from law diminishes with rise of temperature ; thus at temperat above 40° the absorption of sulphur dioxide obeys the law, in the case of ammonia conformity to the law is observed at 1

The gases dissolved by a liquid are not only expelled by boil but are withdrawn by placing the solution in a vacuum. This deed, follows from Henry's law, for if the solubility is proporti to the pressure, and the pressure is nil, the amount of gas disso must also be nil.

The molecules of gas dissolved by a liquid, are regarded as b held by some attractive forces exerted between them and the m cules of the liquid ; in the course of their movements, gas molec are constantly leaving and entering the liquid, and equilibriu established when the same number enter and escape from surface of the liquid in the same time. When the pressure i creased, more gas molecules strike the surface in a unit of time, consequently a greater volume is absorbed. When a solution soluble gas is placed in an atmosphere of another gas, the dissol gas continues to leave the liquid, until equilibrium is establis between the pressure exerted by the gas so leaving, and the am remaining in solution. For this reason a solution of amm when left exposed to the air, rapidly becomes weaker, owin the escape of the dissolved gas into the atmosphere. This pro is accelerated if a stream of less soluble gas be caused to bu through the solution.

**Solubility of Liquids in Liquids.**—The solubility of liquid liquids may be divided into two orders. First, cases in which the degree of solubility of one in the other is unlimited; and, second, cases where the extent of the solubility is limited. Two liquids whose solubility in each other is unlimited, are said to be *miscible in all proportions;* thus alcohol and water are capable of forming a homogeneous mixture when added together in any proportion.

In the second class, where the solubility of two liquids for each other is limited, it is found that each liquid is capable of dissolving some of the other. Thus, if equal volumes of ether and water are shaken together, the liquids will afterwards separate out into two distinct layers, one floating upon the other. The heavier layer at the bottom is an aqueous solution of ether, containing about 10 per cent. of ether; while the upper liquid is an ethereal solution of water, containing about 3 per cent. of water. The presence of ether dissolved in the water may be proved by separating the two layers and gently heating the aqueous liquid in a small flask, when the dissolved ether will be expelled and can be inflamed. The presence of the water, in the ether, is also readily proved, either by introducing into the liquid a small quantity of dehydrated copper sulphate, which will rehydrate itself at the expense of the water in the ether, and be changed from white to blue; or by placing in the ethereal liquid a fragment of sodium, which decomposes the dissolved water with the liberation of hydrogen.

In most cases the solubility of liquids in liquids is increased by rise of temperature, although in some it is decreased.* One notable instance of the latter effect of rise of temperature is seen in the case of a mixture of triethylamine and water. If equal volumes of these liquids be mixed together, at a temperature below 20°, complete solution takes place, and a single homogeneous liquid results. On warming the solution, it becomes turbid, owing to the separation of the liquid into two portions, which ultimately settle out as two distinct layers. As the temperature of the solution approaches 20°, the liquid becomes very sensitive to a slight rise of temperature, the heat of the hand being sufficient to cause turbidity in the solution.

**Solution of Solids in Liquids.**—When a solid is immersed in a liquid, the forces which oppose the solution of the solid are the attractive forces exerted by the molecules of the solid upon each other, and those of the liquid upon themselves. The forces that tend to effect solution are the attractive forces exerted by the molecules of the liquid upon the molecules of the solid, and the kinetic energy of the molecules.

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* See Experiments, Nos. 123 to 128, "Chemical Lecture Experiments," by the author.

By the action of the liquid, the attractive force between the molecules of the solid is diminished, and those molecules nearest the surface, by their own energy and the attraction exerted by the liquid, pass into and through the liquid. In the course of their movements, these sometimes return to the solid, and a condition of equilibrium is finally established, when as many molecules leave the surface of the solid as return to it in a given time. Under these circumstances the solution is said to be *saturated* with respect to the particular solid.

**Saturated Solutions.**—The amount of solid held in solution by the liquid when the latter is saturated, depends upon the temperature, for if the temperature be raised, the kinetic energy of the molecules is increased, and consequently an increased number will become detached from the solid. As a general rule, therefore, the solubility of a solid in a liquid is increased by rise of temperature. A saturated solution at a given temperature may be obtained in two ways, namely, by maintaining the liquid at that temperature and stirring into it an excess of the solid, until no more of it is dissolved; or by dissolving a larger quantity of the solid at a higher temperature, and allowing the solution to stand in contact with an excess of undissolved solid, until the temperature falls to the specified point. During the cooling, the amount of solid that the liquid had taken up, over and above that which was necessary to saturation at the lower temperature, is deposited.

**Supersaturated Solutions.**—The condition of saturation can only be determined when an excess of the undissolved solid is present in the liquid; for when a solution, which is not in contact with any of the undissolved solid, is brought to the point of saturation, either by cooling or by evaporation of the liquid, it frequently happens that no separation of solid takes place. Solutions can in this way be obtained, in which a larger amount of the solid remains dissolved at a given temperature, than corresponds to the amount required to form a saturated solution at that temperature: such solutions are said to be *supersaturated*. If into such a supersaturated solution, a fragment of the solid be introduced, molecules of the dissolved solid at once deposit themselves upon it, and this separation of the dissolved substance continues, until the solution reaches a state of concentration corresponding to its normal saturation at the particular temperature. The introduction into a superurated solution of a particle of the solid, in respect to which the ution is supersaturated, is the only sure method of bringing out the separation of the excess of the dissolved substance ; such olution, therefore, may be preserved for an indefinite time, if it be pt in an hermetically sealed vessel. Minute particles of the solid,

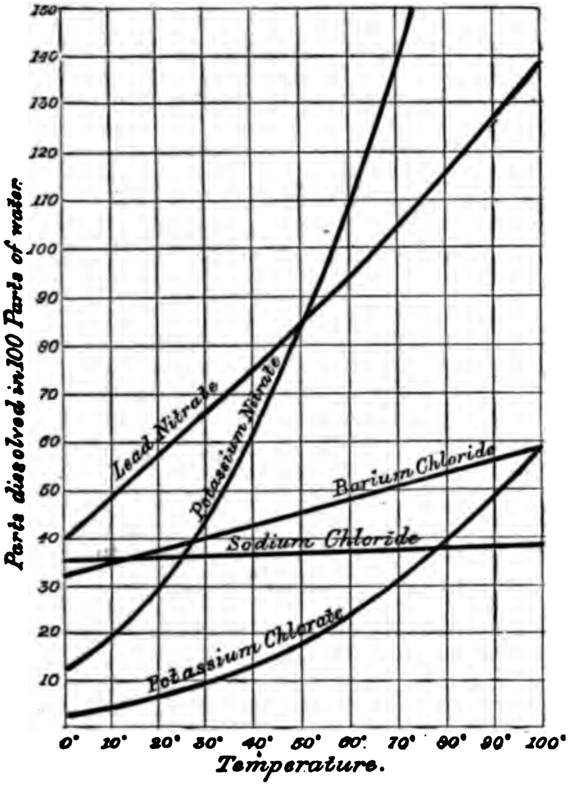

FIG. 20.

ards which a solution is supersaturated, that might be present he dust of the air, falling into such a solution, will determine deposition of the dissolved solid.

he phenomenon of supersaturation is strictly analogous to that of supercooling, or the suspended solidification of fused solids, and is exhibited most readily by salts containing water of crystallisation, such as sodium acetate, $NaC_2H_3O_2,3H_2O$ ; sodium thiosulphate, $Na_2S_2O_3,5H_2O$ ; and sodium sulphate, $Na_2SO_4,10H_2O$. Thus, if a small quantity of water be poured into a flask nearly filled with crystallised sodium thiosulphate (the so-called "Hypo" of the photographer), and the mixture be warmed by immersion in hot water, the whole of the salt will dissolve; and if the solution be then allowed to cool undisturbed, it will assume the ordinary temperature, and still remain fluid. If into this supersaturated solution a crystal of the salt be dropped, the excess of salt present in solution, beyond the normal quantity for saturation at that temperature, will crystallise out, and so great is this excess that the contents of the flask will appear practically solid.

The different solubility of various solids in the same liquid, and the increased solubility by rise of temperature, is graphically shown in Fig. 20, where the solubility curves of five salts in water are represented. The abscissæ indicate temperatures, and the ordinates the number of parts of salt dissolved by 100 parts of water.

Thus at 0°, 100 grammes of water will dissolve 35.7 parts of sodium chloride, and as the temperature is raised, the quantity of salt which the water will dissolve very slowly increases, until at 100° the amount is nearly 40 parts: sodium chloride is therefore nearly equally soluble in water at all temperatures.

In the case of potassium nitrate, 100 grammes of water at 0° will only dissolve 13.3 grammes of the solid, but as the temperature rises the amount capable of being dissolved by this quantity of water very rapidly increases, until at 75° 150 grammes are dissolved. Lead nitrate is more soluble than potassium nitrate between 0° and 50°, but above this point it is not so soluble as the other, hence the two curves intersect at that temperature. The solubility of sodium sulphate in water is anomalous. The solubility at first rapidly increases with rise of temperature from 0°, and reaches a maximum at a point between 33° and 34°, when it gradually diminishes with further rise of temperature. This behaviour is in reality due to the fact that we are not dealing with one and the same substance throughout the experiment. Sodium sulphate exists as a solid in at least three forms, namely, the decahydrate, $Na_2SO_4,10H_2O$ (ordinary Glauber's salt); the heptahydrate, $Na_2SO_4,7H_2O$ ; and the anhydrous salt, $Na_2SO_4$. The first portion of the curve (Fig. 21) represents the solubility of Glauber's salt; thus, at 20° such an ount of this decahydrated salt is dissolved, that the solution tains 20 grammes of $Na_2SO_4$ in 100 grammes of water. The ubility of this salt rapidly rises until 34° is reached, at which perature the salt melts, and is then miscible with water in all

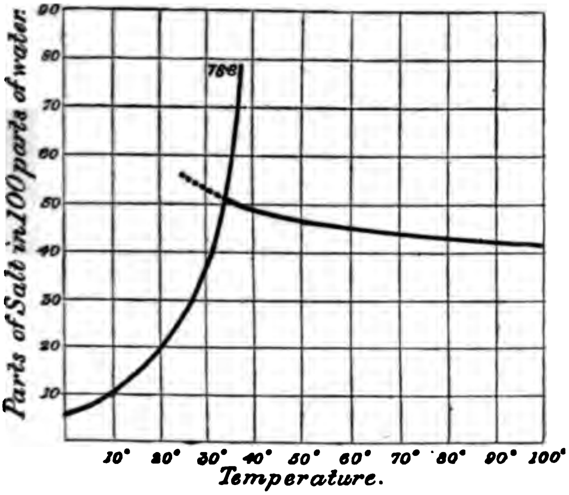

FIG. 21.

portions. The melted salt contains 78.8 parts of $Na_2SO_4$ in parts of water, which is indicated as the highest point upon curve :—

$$\overset{Na_2SO_4.}{\underbrace{23 + 23 + 32 + 64}_{142}} \qquad \overset{10H_2O.}{\underbrace{(2 + 16) \times 10}_{180}} \qquad 180 : 100 = 142 : 78.8.$$

The decahydrated salt is unable to exist, as such, at temperatures gher than 34°, and when the melted salt is heated above this int it is converted into the anhydrous salt, and water satu-ted with the salt; therefore above 34° it is not possible to have solution of sodium sulphate in contact with solid Glauber's lt. It can, however, be in contact with the anhydrous salt, and e second portion of *the curve expresses* the solubility of this compound in water, which slowly diminishes as the temperature rises.

**Osmotic Pressure.**—When a dilute solution of a substance in water is placed in a vessel closed with an animal membrane, such as bladder (M, Fig. 22), and the whole is immersed in water to such a depth that the level of the water outside is coincident with that of the solution within, it is found that the liquid in the inner vessel increases in volume, as seen by the fact that it gradually rises in the narrow stem of the apparatus. Water, therefore, from the outer vessel must have passed in through the membrane, and inasmuch as some of the dissolved substance is found in the water of the outer vessel, some of the solution must at the same time have made its escape through the membrane. After the liquid has risen to a certain height in the narrow tube, it again begins to fall, as the contained solution continues to penetrate the membrane. This process is known as *endosmose*, and the instrument described is called an *endosmometer*.

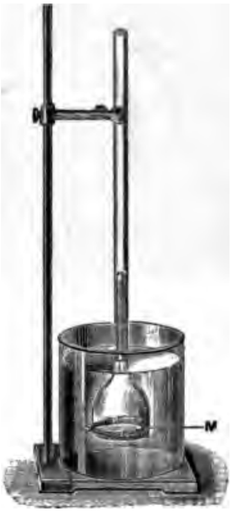

FIG. 22.

Many attempts were made to establish general relations between the height to which the liquid rose in the narrow tube, and the quantities of substance in the solution, but it was found impossible to obtain accurate or comparable measurements, for not only were the results disturbed by the effect of the constantly changing pressure upon the rate at which the dissolved substance escaped through the membrane, but different animal membranes yielded different results.

**Semipermeable Membranes.**—It was first discovered by Traube (1867), and afterwards extended by Pfeffer (1877), that artificial membranes, or pellicles, could be obtained, which, while allowing of the passage of water through them, just as in the case of animal membranes, unlike these materials, they offered a perfect barrier to the passage of many substances in solution in the water. Such pellicles are known as semipermeable membranes. The material that has been found most suitable is precipitated copper ınide. If a solution of copper sulphate ($CuSO_4$) be brought sly in contact with a solution of potassium ferrocyanide $N)_6)$, at the point where the two liquids meet, a film or pellicle ipitated copper ferro- $(Cu_2Fe(CN)_6)$ is pro- In order to make use extremely fragile mem- Pfeffer devised the plan ipitating it within the f a vessel made of un- ɔorcelain. A small clay cal cell, after thorough ıg, was filled with a dilute ı of potassium ferro- , and immersed in dilute sulphate. As these solu- ıtered the pores of the ıd there met, a mem- consisting of copper ınide, was formed within ls, which, under these tances, was sufficiently :o withstand a pressure 5 atmospheres.

:h a cell, furnished with ermeable membrane, be ed as an endosmometer, dilute solution, say of be placed within the us, which is then im- in water, it is found e liquid rises in the tube to a certain height he level of the water in ide vessel, and remains ıary. Water passes ı the membrane, but no d substance passes out. more water penetrates ı, than passes out, hence the increased volume of liquid in ı; *but when a certain pressure* is reached, represented by

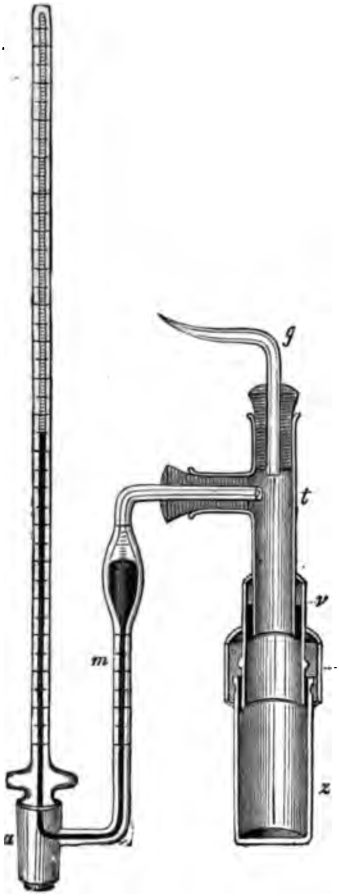

FIG. 23.

poured a quantity of water until the cylinder is nearly full. Upon the top of the water is then floated a solution of potassium thiocyanate in alcohol, and the whole is allowed to remain undisturbed. The ferric chloride will gradually diffuse up into the water, and the dissolved thiocyanate will diffuse down, and at the point where these salts meet they will interact chemically upon each, giving rise to a blood-red coloured solution, which will appear as a ring about midway down the cylinder.

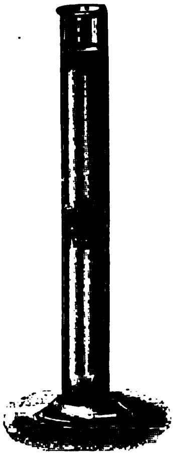

FIG. 24.

This phenomenon of the diffusion of dissolved substances, is strictly comparable with the diffusion of gases, although in the former case the operation proceeds with extreme slowness. The force which impels the molecules of dissolved substances to diffuse, is the osmotic pressure of the substance in solution.

The extension of the gaseous laws into the domain of solutions, necessitates the hypothesis that in the case of some solutions the molecules of the dissolved substance unite to form more complicated molecular associations; while in other cases (including those substances which are electrolytes, such as the solutions of strong acids, bases, and salts) the molecules of the substances undergo dissociation into their *ions* (see Electrolysis, page 93). For, just as in the case of gases, where departures from the strict gaseous laws are seen to take place, on account of the *dissociation* in some instances, and the *association* in others, of the various molecules; so it is believed that the deviations from the strict continuity of the ideal gaseous laws into the realm of solution, are due to the operation of similar causes.

## CRYSTALLINE FORMS.

When a saturated solution of a solid in a liquid, is either cooled or allowed to evaporate, the dissolved solid begins to deposit, and it does so in most cases in definite geometric shapes, termed crystals. (Solids which exhibit no crystalline structure are said to be *amorphous.*)

The same arrangement of molecules into geometric forms often s place when substances in a state of *fusion* (as distinguished *solution*) pass into the solid condition, as, for example, when ed sulphur, or mercury, or water, are cooled to their respective ifying points ; and it also frequently takes place when vapours lense to the solid state.

e more slowly the process of solidification takes place, and arger and more symmetrical are the crystals that are formed. he variety of geometric forms that are met with in naturally rring, and artificially produced, crystals is practically infinite. y are, however, susceptible of a classification, based upon their lopment with respect to certain imaginary planes, called the *es of symmetry*. These are planes cut through the crystal in a manner, that the divided portions are the mirrored reflec- s the one of the other, the mirror being the plane itself. All tals may be referred to one or other of six great families, rding to their symmetry, known as crystallographic systems.

I. The *Regular* system. Crystals belonging to this system have *nine* planes of symmetry, namely, three principal planes at right angles to each other, and six others which intersect one another at angles of 60°. Forms of this system (such, for example, as the *cube*) possess the highest possible order of symmetry.

I. The *Hexagonal* system. Crystals having *seven* planes of symmetry, namely, one principal plane, normal to a vertical axis in the crystal, and six other planes at right angles to the principal plane, and intersecting each other at angles of 30°.

I. The *Quadratic* system. Embracing crystals having *five* planes of symmetry, namely, one principal plane, normal to a vertical axis in the crystal, and four other planes at right angles to the principal plane, and intersecting each other at angles of 45°.

V. The *Rhombic* system. Including crystals having *three* planes of symmetry at right angles to each other.

V. The *Monosymmetric* or *Monoclinic* system. Crystals with only *one* plane of symmetry.

I. The *Asymmetric* or *Triclinic* system. Including crystals which have *no* plane of symmetry. The forms belonging to *this system, having symmetry* with respect to a *point* only.

This system of classification brings the various crystalline forms into direct relations with many of the physical properties possessed by crystals, such, for example, as their optical characters: thus, in the *Regular* system, the crystals in their normal condition are *singly refracting crystals*—they are said to be *isotropic.* In the *Hexagonal* and *Quadratic* systems they are optically *uniaxial;* while in the *Rhombic*, *Monosymmetric*, and *Asymmetric* systems they are all optically *biaxial.*

All crystals may be regarded as derivations from certain typical forms belonging to one of these six systems.* One of the simplest forms of each system is the double pyramid, which in the hexagonal system takes the shape of a double six-sided pyramid, and in the remaining systems that of a double four-sided pyramid, or octahedron. Thus we have the *regular* octahedron, the *quadratic* octahedron, the *rhombic* octahedron, and so on.

By the development of certain related faces, the octahedron passes into the prism, hence we get the *quadratic* prism, the *rhombic* prism, the *hexagonal* prism, &c. It will be obvious, therefore, that the description of a crystal as being *prismatic*, or *octahedral*, in form, is incomplete unless the particular system to which it is referred be also stated.

Crystals, whether naturally occurring or artificially obtained, very seldom exhibit the perfect symmetry of the ideal form. By great care, however, in regulating the formation of a crystal, by the maintenance of a constant temperature, and controlling the rate of evaporation of the solvent, it is possible to cause crystals to grow in such a way, that they will approach very closely to the ideal geometric form. Fig. 140† represents crystals of alum, in the form of *regular* octahedra, or double four-sided pyramids, which were obtained by careful crystallisation from aqueous solution; and it will be seen how near to the ideal they approach. In Fig. 106,† also, are seen illustrations of crystals of sulphur, in the form of *rhombic* octahedra. These crystals were produced by the carefully controlled deposition of the sulphur, from a solution of the element in carbon disulphide, and they illustrate the kind of variations in the form that are introduced by the development of new faces. Fig. 141 † shows a group of naturally occurring crystals, namely, quartz, in the form of *hexagonal* prisms, terminating in hexagonal pyramids.

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* The study of the relations between the various derivatives, and the simpler types, forms a part of the science of crystallography, and falls outside the scope of a general chemical text-book.

† From a photograph of the actual crystals.

In order to determine the system to which a given crystal belongs, it is necessary to make a number of accurate measurements of its angles, and since the inclinations of the faces to one another bear geometric relations to the planes of symmetry, and the inclinations of these planes towards each other, these latter may be calculated from the former values. The instruments by means of which such measures are made are termed goniometers.

Two or more substances which crystallise in the same form are said to be *isomorphous* (see page 49), and, on the other hand, a substance which is capable of crystallising in two forms which do not belong to the same system, is termed a *dimorphous* substance. Thus sulphur is dimorphous, as it is capable of crystallising in the form of *rhombic* octahedra (Fig. 106), and in *monosymmetric* prisms (Fig. 107).

Occasionally a dimorphous substance is isomorphous with another dimorphous body, in both its forms. To this double isomorphism the term *isodimorphism* is applied.

# CHAPTER XV

## *THERMO-CHEMISTRY*

We have seen that by means of symbols and formulæ chemists express, in the form of equations, a certain amount of information respecting chemical changes: thus by the equation $C + O_2 = CO_2$ there are conveyed the facts, that carbon unites with oxygen to form carbon dioxide, that 12 grammes of carbon combine with 32 grammes of oxygen, yielding 44 grammes of carbon dioxide, and that the volume of the gaseous carbon dioxide obtained is the same as that of the oxygen taking part in its formation. All such equations bear upon the face of them the truth, that matter can neither be destroyed nor created. The total *quantity* of matter taking part in the action is unaltered by the process, although it appears in altered form in the products of the reaction.

In all chemical changes, besides matter, *energy* also takes a part; not only do the materials concerned undergo rearrangement, or readjustment, but at the same time there is a rearrangement or readjustment of energy. This energy change is not expressed by the ordinary symbolic equation. Thus in the equation—

$$SO_3 + H_2O = H_2SO_4$$

the fact is embodied that 80 grammes of sulphur trioxide, combine with 18 grammes of water, and form 98 grammes of sulphuric acid; but the equation takes no cognisance of the fact, that when these weights of these two substances unite to form 98 grammes of sulphuric acid, an amount of energy, in the form of heat, is disengaged that would raise the temperature of 213 grammes of water from 0° to the boiling-point.

Similarly, in the equation $2NCl_3 = N_2 + 3Cl_2$ there is no recognition of the fact, that during this change an enormous amount of energy leaves the system in the form of external work,—(overcoming the atmospheric pressure); in other words, that the conversion of nitrogen trichloride into its constituent elements is attended with the most violent explosion.

Energy, like matter, can neither be created nor destroyed, but as a result of chemical action it reappears as energy in another form. Thus it may appear as heat, as electrical energy, as kinetic energy, or as chemical energy; and just as the total amount of *matter* taking part in a chemical change, reappears in altered form in the products of the change, so the disappearance of *energy* in any of its forms, gives rise to the reappearance of a proportionate amount of energy in another form. This is the law of *the conservation of energy*, which may be thus stated:* "*The total energy of any material system, is a quantity which can neither be increased nor diminished by any action between the parts of the system, although it may be transformed into any of the forms of which energy is susceptible.*"

Chemical energy, or that form of energy that is set free during chemical processes, cannot be measured by any direct method. This energy, however, is generally transformed, during chemical change, into heat, and may therefore be measured by, and expressed in, heat units. Thermo-chemistry may therefore be defined as the *science of the thermal changes which accompany chemical changes.*

All matter is regarded as containing a certain amount of energy in some form, and the purpose of thermo-chemistry is, by measuring the thermal disturbance that is conditioned by a chemical change, to ascertain the difference between the amount of energy contained in a system before and after such a change.

If all the energy of a system in its original state (*i.e.*, before the chemical change takes place) that undergoes transformation into other forms of energy, passes into heat; if none of it leaves the system as energy in some other form, and thereby escapes measurement; then the difference between the amount of energy contained in the system in its original and its final state may be ascertained. It by no means follows, however, that this represents the chemical energy alone: it has already been explained that chemical changes are always attended by physical changes, such as change of volume, of physical state, and so on, and we have also learned that such physical changes are likewise accompanied by thermal changes; the problem, therefore, is often a complicated one, and it is not always possible to differentiate between the chemical and the physical causes that may be operating simultaneously, and to decide what share of the final result is due to the chemical phase of the change, and what to the physical change that simultaneously takes place.

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* *Clerk Maxwell*, "Matter and Motion."

As an illustration of the complex nature of chemical reactions when considered from a thermal standpoint, and of the disturbing effect of the accompanying physical changes, we may take the case of the action of aqueous hydrochloric acid, upon crystallised sodium sulphate, $Na_2SO_4,10H_2O$—

$$Na_2SO_4,10H_2O + 2HCl = 2NaCl + H_2SO_4 + 10H_2O.$$

The chemical action here consists of (1) the decomposition of sodium sulphate, (2) the decomposition of hydrochloric acid, (3) the formation of sodium chloride, (4) the formation of sulphuric acid. Heat is absorbed by the first two portions of the action, and heat is evolved by the other two. The physical changes include the passage of ten molecules of water of crystallisation (*i.e.*, *solid* water) into liquid water, and the solution of sodium chloride in water. These changes are attended with absorption of heat, and the net result of the entire change is the disappearance of a considerable amount of heat, that is to say, the thermal value of the reaction is a negative quantity.

The methods adopted in order to express thermo-chemical reactions are quite simple. The ordinary chemical symbols and formulæ are used, and represent, in all cases, quantities in grammes corresponding to the formula-weights of the substances. Thus Cl represents 35.5 grammes of chlorine; $H_2O$ stands for 18 grammes of water, and so on. The chemical equation is followed by a number representing the quantity of heat, expressed in heat units, which is either produced, or which disappears as a result of the change. The unit of heat is the *calorie*, or the quantity of heat that is capable of raising the temperature of 1 gramme of water from 0° to 1°. Sometimes the unit employed is the quantity of heat required to raise 1 gramme of water from 0° to 100°, and this unit (which is 100 times greater than the calorie) is indicated usually by the letter K. When heat is produced by a chemical change, the sign + is placed in front of the number of units, and when heat disappears, the fact is indicated by the sign −.

Thus the equation—

$$H_2 + Cl_2 = 2HCl + 44{,}000 \text{ cal.}$$

or

$$H_2 + Cl_2 = 2HCl + 440 \text{ K},$$

means that when 2 grammes of hydrogen combine with 71 grammes of chlorine to form gaseous hydrochloric acid, heat is disengaged to the amount of 44,000 calories, or 440 of the larger units, K. Or, in other words, that when these quantities of these substances combine, an amount of energy is lost to the system, represented by 44,000 calories. Therefore the energy possessed by 2 grammes of hydrogen and 71 grammes of chlorine is greater than that possessed by 73 grammes of hydrochloric acid gas by an amount which is represented by 44,000 gram-units of heat. Hence the equation may be written—

$$\mathrm{2HCl} = \mathrm{H_2} + \mathrm{Cl_2} - 44{,}000 \text{ cal.}$$

which signifies that when 73 grammes of gaseous hydrochloric acid are decomposed into chlorine and hydrogen, jt is necessary to supply an amount of energy equal to 44,000 calories.

In order to indicate the state of aggregation of the different substances, the method introduced by Ostwald consists in the use of different type, thick type being employed to denote solids, ordinary type indicating liquids, and italics signifying gases, thus—

$$\mathbf{C} + O_2 = CO_2 + 97{,}000 \text{ cal.}$$

means that the total energies of 12 grammes of solid carbon and 32 grammes of gaseous oxygen is greater than the energy possessed by 44 grammes of gaseous carbon dioxide by an amount equivalent to 97,000 calories.

Or, again, the equation—

$$\mathbf{SO_3} + \mathrm{H_2O} = \mathrm{H_2SO_4} + 21{,}320 \text{ cal.}$$

signifies that 80 grammes of solid sulphur trioxide unites with 18 grammes of liquid water, and forms 98 grammes of liquid sulphuric acid, with the liberation of 21,300 gram-units of heat.

Similarly the heat evolved by the passage of water into ice, and the heat that disappears when water passes into steam, may be expressed by the equations—

$$\mathrm{H_2O} = \mathbf{H_2O} + 1440 \text{ cal.}$$
$$\mathrm{H_2O} = H_2O - 9670 \text{ cal.}$$

when water *takes a direct part in* the chemical change, as, for example, in the action of sulphur trioxide and water already quoted, the formula represents a gram-molecule just as in all other cases; but where the presence of a large quantity of water affects the thermal result of the chemical change, by exerting, for example, a solvent action, the symbol Aq is employed to signify that the presence of the water is considered in the thermal expression.

Thus the expression—

$$HBr + \mathrm{Aq} = \mathrm{HBrAq} + 19{,}900 \text{ cal.}$$

signifies that when 81 grammes of gaseous hydrobromic acid are dissolved in a large excess of water, 19,900 calories are evolved.

Again, the equation—

$$H_2 + Br_2 + \mathrm{Aq} = 2\mathrm{HBrAq} + 64{,}000 \text{ cal.}$$

means that when 160 grammes of gaseous bromine combine with 2 grammes of hydrogen, and the product is dissolved in an excess of water (*i.e.*, such a quantity of water that no thermal change is produced by the addition of any further quantity), 64,000 calories are disengaged. Of this 64,000 calories, 19,900 × 2 = 39,800 are due to the solution of the twice 81 grammes of hydrobromic acid, and the difference, viz., 24,000 calories, represent the heat produced by the combination of 2 grammes of hydrogen with 160 grammes of bromine.

If water is formed as one of the products of the chemical reaction taking place in the case of substances in aqueous solution, such as when a solution of hydrochloric acid is added to a solution of sodium hydroxide, $\mathrm{HCl} + \mathrm{NaHO} = \mathrm{NaCl} + \mathrm{H_2O}$, as the water so produced simply mixes with the water in which the materials are dissolved, without producing any thermal effects, it is usually neglected in energy equations. Thus the above action may be expressed—

$$\mathrm{HClAq} + \mathrm{NaHOAq} = \mathrm{NaClAq} + 13{,}736 \text{ cal.}$$

The heat that is produced, or that disappears, in a chemical change which results in the formation of a particular compound, is termed the *heat of formation* of that compound. Thus in the equation—

$$H_2 + Cl_2 = 2HCl + 44{,}000 \text{ cal.}$$

the heat of formation of 73 grammes of hydrochloric acid is 44,000 thermal units. This number, however, is in reality the algebraic sum of three quantities. It does not express merely the heat developed by the simple union of chlorine and hydrogen. The chemical change expressed by the equation consists in reality of three operations—

(1.) $H_2 = H + H$. (2.) $Cl_2 = Cl + Cl$. (3.) $Cl + Cl + H + H = 2HCl$.

Each of these operations represents a distinct thermal effect; in Nos. (1) and (2) heat is absorbed, in No. (3) heat is evolved, and calling these values $h_1$, $h_2$, and $h_3$, we have as the net result $h_3 - (h_1 + h_2) = 44{,}000$ cal.

The number of heat-units, therefore, which expresses the heat of formation of hydrochloric acid, is the heat produced by the union of two atoms of hydrogen with two atoms of chlorine, minus the heat absorbed in the decomposition of one hydrogen and one chlorine molecule.

Compounds such as hydrochloric acid, in the formation of which heat is developed, are termed *exothermic* compounds, the reaction by which they are produced being an exothermic change; compounds, on the other hand, whose heats of formation are expressed by a negative sign, that is, in whose formation heat disappears, are distinguished as *endothermic compounds*, and the reactions by which they are formed are endothermic reaction.

Thus $$C + S_2 = CS_2 - 19{,}600 \text{ cal.},$$

signifies that in the formation of carbon disulphide, heat is absorbed, and the compound is therefore an endothermic compound.

Thermo-chemical determinations are made by means of instruments termed calorimeters. These are of great variety, although the principle involved is the same. The chemical reaction is caused to take place under such circumstances, that the whole of the heat that is liberated shall be communicated to a known volume of water, at a known temperature.*

Direct determinations of the thermal value of chemical changes, have hitherto been made in only a limited number of comparatively simple cases: it is possible, however, from a few known data, to calculate the thermal values of a number of changes which cannot be directly measured. This depends upon the fundamental principle of thermo-chemistry, which is itself the corollary of the law of the conservation of energy, and which was first experimentally proved by Hess (1840). This principle, which is sometimes termed the ***law of constant heat consummation***, or the ***law of equivalence of heat and chemical change***, may be thus stated: The amount of heat that is liberated, or absorbed, during a chemical process, is dependent solely upon the initial and final states of the system, and is independent of the intermediate stages. The following examples will serve to explain the application of the principle :—

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* For descriptions of the various calorimeters, see Treatises on Physics.

1. Let us suppose it is desired to find the heat of formation of carbon monoxide, the data at our disposal being (1) the heat produced when carbon unites with oxygen to form carbon dioxide; and (2) the heat formed by the combustion of carbon monoxide to carbon dioxide. The thermal equations are—

$$(1)\ C + O_2 = CO_2 + 97{,}000 \text{ cal.}$$

$$(2)\ 2CO + O_2 = 2CO_2 + 136{,}000 \text{ cal.}$$

Halving the second equation, in order to get the heat produced in the formation of 44 grammes of carbon dioxide (*i.e.*, the same weight as in the first), we may represent the equation as—

$$CO + O = CO_2 + 68{,}000 \text{ cal.*}$$

The difference between the two values 97,000 and 68,000 will be the heat of formation of carbon monoxide, therefore we get the equation—

$$C + O = CO + 29{,}000 \text{ cal.}$$

2. The compound, methane (marsh gas), $CH_4$, cannot be formed by the direct union of its elements, but its heat of formation can be calculated by the application of this principle. The data in this case are the ascertained heats of formation of carbon dioxide

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* It must be remembered that this equation does not express the whole truth: as it here stands it would imply that 68,000 calories represent the heat formed by the simple chemical union of 28 grammes of carbon monoxide with 16 grammes of oxygen. In reality this number is half the sum of the two values, namely, the heat of combination of 56 grammes of carbon monoxide with 32 grammes of oxygen, *minus* the heat absorbed by the decomposition of 32 grammes of oxygen molecules into their constituent atoms. The oxygen atom does not exist alone, and whenever free oxygen takes part in a chemical change, the molecules of the element are first separated into their atoms.

and of water, and the heat produced by the combustion of marsh gas, the thermal equations being—

(1) $C + O_2 = CO_2 + 97{,}000$ cal.
(2) $2H_2 + O_2 = 2H_2O + 136{,}800$ cal.
(3) $CH_4 + 2O_2 = CO_2 + 2H_2O + 212{,}000$ cal.

The difference between the thermal value of the last process, and the sum of the first and second, represents the heat of formation of marsh gas—

$$97{,}000 + 136{,}800 - 212{,}000 = 21{,}800,$$

hence we get the expression—

$$C + 2H_2 = CH_4 + 21{,}800 \text{ cal.}$$

# PART II

## THE STUDY OF FOUR TYPICAL ELEMENTS

### HYDROGEN—OXYGEN—NITROGEN—CARBON

AND THEIR MORE IMPORTANT COMPOUNDS

## CHAPTER I

### *HYDROGEN*

Symbol, H. Atomic weight = 1. Molecular weight = 2. Density = 1.

**History.**—The existence of hydrogen as an individual substance was first established by Cavendish (1766), who applied to it the name *inflammable air*. He obtained the gas by acting upon certain metals, as iron, tin, and zinc, with either sulphuric or hydrochloric acid.

**Occurrence.**—In the free state hydrogen occurs only in small quantities upon the earth. It is evolved with other volcanic gases, and is present in the gases which escape from petroleum wells. It is evolved also during the fermentation and decomposition of certain organic compounds, and is therefore present in the breath and the intestinal gases of animals. Hydrogen has also been found in many specimens of meteoric iron, where it is present as *occluded* gas.

Hydrogen in the uncombined state exists in enormous masses upon the sun, and is present in certain stars and nebulæ. The so-called *prominences* which are seen projecting from the sun's disk to a distance of many thousands of miles, and which were first observed during solar eclipses, consist of vast masses of incandescent hydrogen.

In combination with other elements hydrogen is extremely abundant: its commonest compound is water, which consists of one part by weight of this element combined with eight parts of oxygen. In combination with chlorine, as hydrochloric acid, with carbon as marsh gas, and with sulphur as sulphuretted hydrogen, this element also occurs in large quantities. All known acids contain hydrogen as one of their constituents, and it is present in almost all organic compounds.

**Modes of Formation.**—(1.) Hydrogen may be obtained from

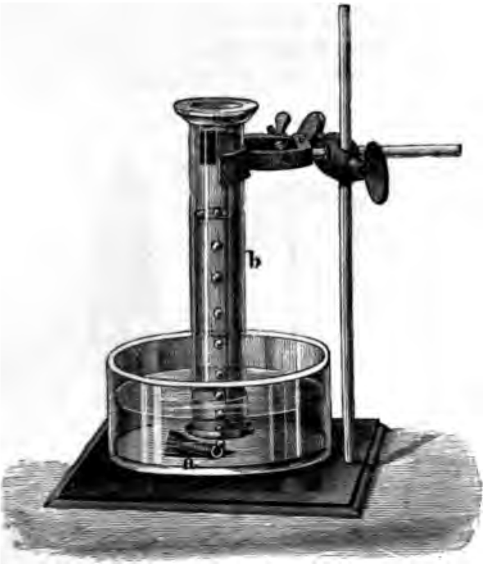

FIG. 25.

water by the action of various metals upon that compound under certain conditions. The metals sodium and potassium will decompose water at the ordinary temperatures; when, therefore, a fragment of either of these metals is thrown upon water, the latter is decomposed, and hydrogen set free:—

$$H_2O + Na = NaHO + H.$$

The metals being lighter than water float upon its surface, and, owing to the heat of the reaction, melt and roll about upon the liquid as molten globules. *With potassium,* the heat developed is sufficiently great to cause the hydrogen to inflame, and it burns with a flame coloured violet by the vapour of the metal. The hydroxide of the metal, which is the second product of the action, dissolves in the excess of water, rendering the liquid alkaline. The alkalinity of the solution may be made evident by the addition of a reddened solution of litmus, which will be turned blue by the alkali.

In order to collect the hydrogen evolved by the action of sodium upon water, the metal is placed in a short piece of lead tube closed at one end, which causes it to sink in the liquid, and an inverted glass cylinder filled with water is placed over it, as shown in Fig. 25.

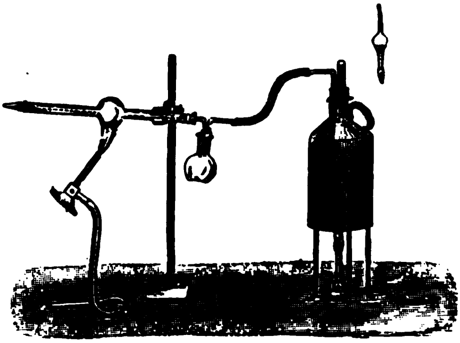

FIG. 26.

The evolved hydrogen then rises as a stream of bubbles into the cylinder and displaces the water.*

(2.) Water may be readily decomposed at the boiling-point, by means of zinc, if the metal be previously coated with a thin film of copper by immersion in a dilute solution of copper sulphate. When this copper-coated zinc (known as zinc-copper couple) is heated in a small flask filled with water, and provided with a delivery tube, the oxygen of the water combines with the zinc forming zinc oxide, and hydrogen is evolved, which may be collected over water at the pneumatic trough: *—

$$Zn + H_2O = ZnO + H_2.$$

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* For detailed description of these experiments see Newth's "Chemical Lecture Experiments," p. 2.

3. At a still higher temperature, water in the state of steam can be readily decomposed by the metal magnesium, magnesium oxide being formed and hydrogen liberated :—

$$Mg + H_2O = MgO + H_2.$$

For this purpose the magnesium is strongly heated in a glass bulb (Fig. 26), while steam from a small boiler is passed over it. As the temperature of the metal approaches a red heat it bursts into flame, and the issuing hydrogen may be ignited as it escapes from the end of the tube.

(4.) If iron be heated to bright redness, and steam be passed over it, the water is decomposed, the oxygen uniting with the iron to form an oxide known as triferric tetroxide, or *magnetic oxide of iron*, thus—

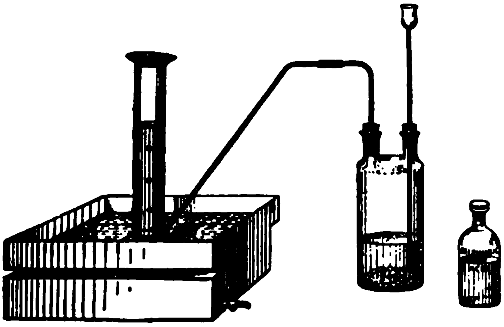

FIG. 27.

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

This method is employed on a large scale for the preparation of hydrogen for commercial purposes. Iron borings or turnings are packed into an iron tube, which is strongly heated in a furnace, and steam from a boiler is passed through the tube.

(5.) For laboratory purposes hydrogen is most conveniently prepared by the action of dilute sulphuric acid upon zinc :—

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

For *this purpose granulated* zinc (*i.e.*, zinc which has been melted and poured into water) is placed in a two-necked Woulf's bottle (Fig. 27), and a quantity of sulphuric acid, previously diluted with six times its volume of water, is introduced by means of the funnel. A brisk action sets in, and hydrogen is rapidly disengaged. After the lapse of a few minutes, the air within the apparatus will be swept out by the hydrogen, when the gas may be collected over water in the pneumatic trough.

The hydrogen so obtained is never absolutely pure: it is liable to contain traces of arsenuretted hydrogen, sulphuretted hydrogen, phosphoretted hydrogen, oxides of nitrogen, and nitrogen. The nitrogen is derived from the air, which finds its way through joints in the apparatus, and also from air dissolved in the acid. There is no known process for removing this impurity. The other gases are due to impurities in the zinc and the sulphuric acid, and can be removed, if required, by passing the hydrogen through a series of tubes containing absorbents (see p. 187).

Absolutely pure sulphuric acid, even when diluted with water, has no action upon perfectly pure zinc.

Scrap iron may be substituted for zinc, but the hydrogen so obtained is much less pure, and is accompanied by compounds of carbon (derived from the carbon in the iron), which impart to the gas an unpleasant smell; the reaction in this case is the following:—

$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

Hydrochloric acid can be employed in place of sulphuric acid with either zinc or iron, the reaction then being:—

$$Zn + 2HCl = ZnCl_2 + H_2.$$

(6.) Hydrogen in a high degree of purity is conveniently prepared in small quantity by the electrolysis of water acidulated with sulphuric acid (see p. 183).

(7.) Hydrogen is disengaged when certain metals, such as zinc, iron, magnesium, and aluminium, are boiled with an aqueous solution of potassium or sodium hydroxide. Thus, in the case of zinc, when this metal in the form of filings is boiled with a solution of potassium hydroxide, hydrogen is evolved, and a compound of zinc, potassium, and oxygen remains in solution, namely, potassium zinc oxide, thus:—

$$2KHO + Zn = H_2 + ZnK_2O_2.$$

(8.) Hydrogen is also obtained by heating alkaline oxalates, or nates, with either potassium or sodium hydroxide, with the ultaneous formation of an alkaline carbonate ; thus with sodium late :—

$$Na_2C_2O_4 + 2NaHO = H_2 + 2Na_2CO_3.$$

**'roperties.**—Hydrogen is a colourless gas, and has neither :e nor smell. It is the lightest known substance, being 14.435 es lighter than air. Its specific gravity is 0.0693 (air = 1). e litre of the gas at 0° C., and under a pressure of 760 mm. of rcury (*i.e.*, the standard temperature and pressure), weighs 896 gramme ; or 1 gramme of hydrogen at the standard temature and pressure occupies 11.165 litres.

)n account of its extreme lightness, hydrogen may be poured

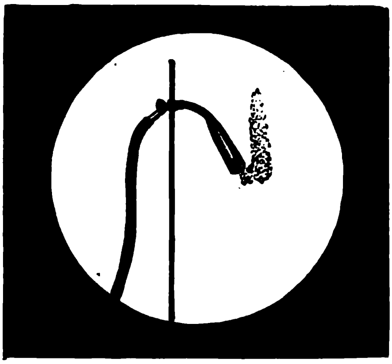

FIG. 28.

*vards* from one vessel to another. If a large beaker be susided mouth downward from the arm of a balance, and countersed, and the contents of a jar of hydrogen be poured upwards ) the beaker, the equilibrium of the system will be disturbed, l the arm carrying the beaker will rise.

:he lightness of hydrogen can also be shown, by causing a :am of the gas to issue from a tube placed in such a position t its shadow is cast upon a white screen by means of a powerful :tric light. When the gas is streaming from the tube, its up:d rush will be visible upon the screen as a distinct shadow, sed by the difference between the refractive power of air and lrogen *(Fig. 28).*

Hydrogen is inflammable, and burns with a non-luminous flame, the temperature of which is very high. The product of the combustion of hydrogen is water, and if a jet of the gas be burned beneath the apparatus seen in Fig. 29, considerable quantities of water may be collected in the bulb. In the act of combustion, the hydrogen combines with the oxygen of the air, forming the oxide of hydrogen, namely, water: *—

$$H_2 + O = H_2O.$$

If hydrogen be mixed with the requisite quantity of air, or oxygen, and a light applied to the mixture, the combination of the two gases takes place instantly, with a violent explosion; hence the necessity of carefully expelling all the air from the apparatus in which hydrogen is being generated, before applying a flame to the issuing gas.

Hydrogen will not support the combustion of ordinary combustibles; thus, if a burning taper be thrust into a jar of the gas, the hydrogen itself will be ignited at the mouth of the jar, which must be held in an inverted position, but the taper will be extinguished; on withdrawing the taper it may be re-ignited by the burning hydrogen.

Although hydrogen is not poisonous, it is incapable of supporting animal life owing simply to the exclusion of oxygen. When mixed with air and inhaled, it raises the pitch of the voice almost to a falsetto. The same effect may be seen by sounding a pitch-pipe, or organ-pipe, by means of a stream of hydrogen instead of ordinary air, when it will be noticed that the note given out is greatly raised in pitch.

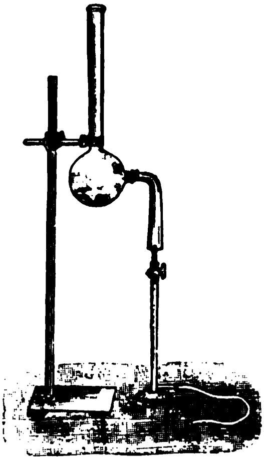

FIG. 29.

Hydrogen is very slightly soluble in water. It was formerly believed that this gas formed an exception to the rule that the solubility of gases in water diminishes with rise of temperature, and it was supposed that the solubility of hydrogen was constant between the temperatures 0° and 25°. More recent experiments

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* *From this fact the name* Hydrogen (signifying *the water producer*) is derived.

have shown that this is not the case. The solubility of this gas, as determined by W. Timofejeff (1890), is seen in the following table:—

*Solubility of Hydrogen in Water.*

| Temperature. | Coefficient of Solubility. |
|---|---|
| 0° | .0215 |
| 10° | ,0198 |
| 20° | .0184 |
| 25° | .0174 |

Hydrogen is the only known gas which has never been liquefied. Up to the present time (1894) this gas has resisted all attempts to liquefy it. The statements that are current as to its liquefaction are founded on imperfect experiment.

**Hydrogenium.**—Certain metals, such as iron, platinum, and notably palladium, possess the property when heated of absorbing a large quantity of hydrogen, and of retaining it when cold. Graham found that at a red heat palladium absorbed, or *occluded*, about 900 times its own volume of hydrogen, while even at ordinary temperatures it was able to absorb as much as 376 times its volume.* Graham concluded that the hydrogen so occluded assumed the solid form, and was alloyed with the palladium, and to denote the metallic nature of the gas he gave to it the name *hydrogenium*. From recent experiments of Troost and Hautefeuille, it seems probable that a definite compound of hydrogen and palladium exists, of the composition $PdH_2$.

The absorption of hydrogen by palladium is readily seen, by making a strip of palladium foil the negative electrode in an electrolytic cell containing acidulated water, the positive pole being of platinum. Oxygen will be evolved from the latter electrode, while for some time no gas will be disengaged from the surface of the palladium, the hydrogen being completely absorbed by the metal. During the absorption of hydrogen the palladium undergoes an increase in volume: Graham observed the

* According to Neumann and Strientz (*Zeitschrift für Analytische Chemie*, vol. 32), one volume of various metals in a fine state of division are capable of absorbing the following amounts of hydrogen:—

| | | | |
|---|---|---|---|
| Palladium, black | 502.35 vols. | Nickel | 17.57 vols. |
| Platinum, sponge | 49.3 ,, | Copper | 4.5 ,, |
| Gold | 46.3 ,, | Aluminium | 2.72 ,, |
| Iron | 19.17 ,, | Lead | 0.15 ,, |

increase in length of a palladium wire, to be equal to 1.6 per ce
This change in volume suffered by the metal may be striking
demonstrated by employing two strips of palladium foil, protect
on one side by a varnish, as the electrodes in the electrolytic ce
On passing the current the negative electrode immediately begi
to bend over towards the varnished side: when the current i
reversed it again uncurls; and the other, being now the negativ
pole, at once begins to perform the same curling movements.

Hydrogenium is capable of bringing about a number of chemical changes which ordinary hydrogen is unable to effect: thus, when a strip of hydrogenised palladium is immersed in a solution of a ferric salt, a portion of the iron is reduced to the ferrous state.*

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* See "Chemical Lecture Experiments," Nos. 27, 28, 29.

# CHAPTER II

## OXYGEN

**Symbol. O.** Atomic weight = 15.96. Molecular weight = 31.92.

**istory.**—**Oxygen** was discovered by Priestley (1774). He obied it by heating the red oxide of mercury (known in those days *mercurius calcinatus, per se*) by concentrating the sun's rays on it by means of a powerful lens. Priestley applied to the gas e name *dephlogistigated air.* Oxygen was independently disovered by Scheele. Scheele's discovery of oxygen was published n 1775, but recent research among his original papers, has brought o light the fact that the discovery was actually made in 1773, prior herefore to Priestley's discovery. Scheele called the gas *empyreal ir*, on account of its property of supporting combustion. Lavoisier subsequently applied to this gas the name "oxygene" (from ὀξύς, sour; and γεννάω, I produce), to denote the fact that in many instances, the products obtained by the combustion of substances in the gas were endowed with acid properties. Oxygen, indeed, came to be regarded as an essential constituent of acids, and was looked upon as the "acidifying principle." The subsequent development of the science has shown that this idea is erroneous, and that oxygen is not a necessary constituent of all acids.

**Occurrence.**—In the free state oxygen occurs in the atmosphere, mechanically mixed with about four times its volume of nitrogen. In combination with other elements it is found in enormous quantities. Thus it constitutes eight-ninths by weight of water, and nearly one-half by weight of the rocks of which the earth's crust is mainly composed.

The following table (Bunsen) gives the average composition of the earth's solid crust, so far as it has been penetrated by man. It must be remembered, however, that the greatest depth to which man has examined, when compared with the diameter of the earth, is after all only, as it were, a mere scratch.

*Average Composition of the Earth's Crust.*

| | | | |
|---|---|---|---|
| Oxygen | 44.0 | to | 48.7 |
| Silicon | 22.8 | „ | 36.2 |
| Aluminium | 9.9 | „ | 6.1 |
| Iron | 9.9 | „ | 2.4 |
| Calcium | 6.6 | „ | 0.9 |
| Magnesium | 2.7 | „ | 0.1 |
| Sodium | 2.4 | „ | 2.5 |
| Potassium | 1.7 | „ | 3.1 |
| | 100.00 | | 100.00 |

**Modes of Formation.**—(1.) Oxygen may readily be obtained by a slight modification of Priestley's original method, namely, by heating mercuric oxide in a glass tube, by means of a Bunsen flame. The red oxide of mercury first darkens in colour, and is decomposed by the action of the heat into mercury and oxygen, thus—

$$2HgO = 2Hg + O_2.$$

The evolved oxygen may be collected over water in the pneumatic trough, while the mercury condenses in the form of metallic globules upon the cooler parts of the tube. This method of obtaining oxygen is never employed when any quantity of the gas is required—it is chiefly of historic interest.

(2.) For experimental purposes, oxygen is best prepared from potassium chlorate. When this salt is heated it melts, and at about 400° decomposes with brisk effervescence due to the evolution of oxygen, while potassium chloride remains :*—

$$KClO_3 = KCl + 3O.$$

If the potassium chlorate be previously mixed with about one-fourth of its weight of manganese dioxide, it gives up the whole of its oxygen at a temperature considerably below the melting-point of the salt, and at a greatly accelerated rate. When, therefore, the oxygen is not required to be perfectly pure, a mixture of these two substances is usually employed. The mixture may be conveniently heated in a "Florence" flask, supported in the position shown in the figure, and gently heated with a Bunsen flame. The gas is washed by being passed through water, and then collected either at the pneumatic trough or in a gas-holder.

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* The mechanism of this reaction is more complex than is represented by this equation. It has been shown that during the decomposition, potassium perchlorate, $KClO_4$, is continuously being formed, and again resolved into $KClO_3$ and O.

The manganese dioxide is found at the end of the reaction to be unchanged: the part it plays in the decomposition belongs to a class of phenomena to which the name *catalysis* is applied; the manganese dioxide, in this instance, being the *catalytic agent.* It was at one time supposed that by its mere presence, itself undergoing no change, the manganese dioxide enabled the potassium chlorate to give up its oxygen more readily and at a lower temperature; but the accumulated evidence which has been collected by the study of an increasing number of similar cases of catalytic action, leads to the conclusion that the manganese dioxide is here playing a more distinctly chemical part in the reaction. So far as is known, in all phenomena of this order, the catalytic agent is a substance which possesses a certain degree of chemical affinity for one of the constituents of the body to be decomposed, and the influence of this attraction is a necessary factor in determining the splitting up of the compound. Owing, however, to certain conditions which are present, such, for example, as the particular temperature at which the reaction is conducted, the catalytic agent is unable to actually combine with the constituent for which it has this affinity, or if it combines, the combination it forms is unable to exist, and is instantly resolved again: hence the catalytic agent comes out of the action in the same state as it was at the commencement.

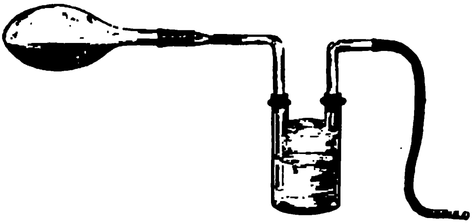

FIG. 30.

In the case before us, it is believed that a cycle of changes takes place,[*] in which the power possessed by manganese to enter into higher states of oxidation, results first in the formation of potassium permanganate, $KMnO_4$; with the simultaneous production of chlorine and oxygen, thus—

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[*] *M'Leod.*

$$(1)\ 2MnO_2 + 2KClO_3 = 2KMnO_4 + Cl_2 + O_2.$$

The potassium permanganate then passes into potassium manganate, $K_2MnO_4$, with evolution of oxygen, and partial reformation of manganese dioxide, thus—

$$(2)\ 2KMnO_4 = K_2MnO_4 + MnO_2 + O_2.$$

And this is decomposed, by the chlorine evolved by the first reaction, into potassium chloride, manganese dioxide, and oxygen, thus—

$$(3)\ K_2MnO_4 + Cl_2 = 2KCl + MnO_2 + O_2.$$

(3.) When manganese dioxide itself is heated to bright redness, it parts with one-third of its oxygen, and is converted into trimanganic tetroxide.

$$3MnO_2 = Mn_3O_4 + O_2.$$

(4.) Other peroxides, when heated, similarly yield a portion of the oxygen they contain. One of these, namely, barium peroxide, is now largely employed for the preparation of oxygen upon a manufacturing scale. This method, known as *Brins'* process, from the name of the inventor, is based upon the fact, that when barium oxide (BaO) is heated in contact with air, it unites with an additional atom of oxygen, forming barium peroxide, thus—

$$BaO + O = BaO_2.$$

And that when this substance is still further heated, it again parts with the additional oxygen and is reconverted into the monoxide—

$$BaO_2 = BaO + O.$$

The process, therefore, is only an indirect method of obtaining oxygen from the air, the same quantity of barium monoxide being employed over and over again. In practice it was found, that instead of effecting the two reactions by altering the temperature, which involved loss of time and considerable expense, the same result could be obtained by altering the *pressure* and keeping the temperature constant. If the monoxide be heated to the lower temperature, at which the first reaction takes place, and air be passed over it at the ordinary atmospheric pressure, atmospheric oxygen is taken up and barium peroxide is formed. If the pressure be then slightly reduced by suitable exhaust pumps, the peroxide immediately gives up one atom of oxygen without any further application of heat, and is retransformed into the monoxide. In this way, by alternately sending air through the heated retorts containing the oxide, and then exhausting the retorts, a continuous process is obtained without change of temperature.

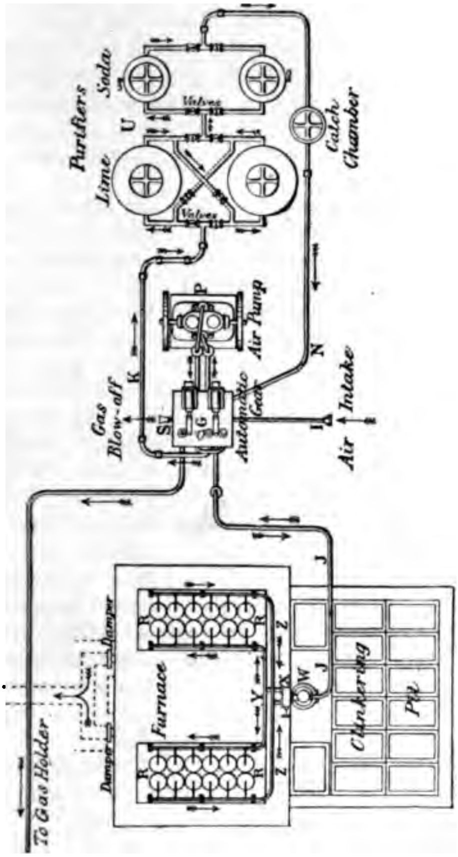

FIG. 31.

The *modus operandi* of the process will be seen from Fig. 31, which represents the general arrangement of the apparatus. A number of retorts, R, consisting of long narrow iron pipes, are arranged vertically in rows in the furnace, where they are heated by means of "producer-gas" (*i.e.* carbon monoxide with atmospheric nitrogen, obtained by the regulated combustion of coke).

By means of the pump P, air is drawn in at the "air intake," and forced through purifiers in order to withdraw atmospheric carbon dioxide; the complete removal of this impurity being essential to the successful carrying out of the operation. The purifiers are so arranged, that any of them can be thrown out of use at will.

By means of automatic gear the purified air is sent through pipe J to the distributing valve X, from which it passes by the pipe Y into the retorts, being made to pass down through one row, and up through the other. The oxygen is then absorbed, and the accumulating nitrogen escapes by the relief valve W. When the absorption of oxygen by the barium monoxide in the retorts has continued for ten or fifteen minutes, the automatic reversing gear comes into operation. The relief valve W is thereby closed, communication with the purifiers is cut off, and the action of the pumps at once causes a reduction of pressure within the retorts. When the pressure falls to about 660 mm. (26 inches, or about 13 lbs. on the square inch), the peroxide gives up oxygen, and is reduced to the monoxide. The oxygen is drawn away by the pipe J and is passed on to a gas-holder. The first portions of gas that are drawn out of the retorts, will obviously be mixed with the atmospheric nitrogen which was there present; in order that this shall be got rid of, the automatic gear is so arranged, that communication with the pipe leading to the gas-holder is not opened until a few seconds after the reversing gear is in operation, and the first portions of gas that are pumped out, are made to escape into the air by a snifting valve S, which is automatically opened and closed.

(5.) Oxygen may be obtained by heating manganese dioxide with sulphuric acid, the dioxide parting with the half of its oxygen, and a sulphate of the lower oxide being formed—

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$

(6.) Similarly, potassium dichromate (a salt containing chromium trioxide, $CrO_3$), when heated with sulphuric acid, yields oxygen; the chromium at the same time being reduced to a lower state of oxidation, viz., $Cr_2O_3$, in which condition it unites with sulphuric acid, forming chromium sulphate—

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O.$$

During the reaction, the red colour of the dichromate changes to the deep olive-green colour possessed by chromium sulphate.

(7.) Many other highly oxidised salts yield oxygen when acted upon by sulphuric acid; thus, with potassium permanganate, the following action takes place:—

$$K_2Mn_2O_8 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$

(8.) If hydrogen peroxide be added to dilute sulphuric acid, and the mixture dropped upon a solution of potassium permanganate contained in a suitable generating flask, a rapid evolution of oxygen takes place at the ordinary temperature, thus—

$$K_2Mn_2O_8 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

(9.) When strong sulphuric acid is dropped upon fragments of brick or pumice-stone, contained in an earthenware or platinum retort, and maintained at a bright red heat, the acid is decomposed into water, sulphur dioxide, and oxygen—

$$H_2SO_4 = H_2O + SO_2 + O.$$

The products of the decomposition are passed through water, which absorbs the sulphur dioxide, and also arrests any undecomposed sulphuric acid, and the oxygen is collected over water. When this process is used on a large scale, the sulphur dioxide is absorbed by being passed through a tower filled with coke, and down which a stream of water is allowed to trickle, and the solution so obtained can be utilised in the manufacture of sulphuric acid.

(10.) Oxygen can be obtained from bleaching-powder by methods which afford interesting instances of catalytic action.* The composition of bleaching-powder is expressed by the formula $Ca(OCl)Cl$. If this substance be mixed with water, and a small quantity of precipitated cobalt oxide added, and the mixture gently warmed, oxygen is rapidly evolved. The cobalt oxide, $CoO$, is the catalytic agent; it is able to combine with more oxygen to form

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* *Experiments 34, 35, 36,* "Chemical Lecture Experiments."

$Co_2O_3$, but this compound is reduced as fast as it is formed, and the oxygen is evolved as gas—

(1.) $Ca(OCl)Cl + 2CoO = Co_2O_3 + CaCl_2$.

(2.) $Co_2O_3 = 2CoO + O$.

A solution of calcium hypochlorite, which may be obtained from bleaching-powder (see Bleaching-powder), behaves in the same way; and, as in the above reaction, nickel oxide may be substituted for cobalt—

$$Ca(OCl)_2 = CaCl_2 + O_2.$$

(11.) A similar instance of catalysis, by which oxygen may be obtained, is seen when a stream of chlorine gas is passed through boiling milk of lime, to which a small quantity of the oxide of cobalt or nickel has been added—

$$CaH_2O_2 + Cl_2 = CaCl_2 + H_2O + O.$$

A reaction of the same order takes place, when the milk of lime is replaced by either potassium or sodium hydroxide—

$$2NaHO + Cl_2 = 2NaCl + H_2O + O.$$

(12.) When a mixture of steam and chlorine gas is heated to bright redness, the steam is decomposed, the hydrogen combining with the chlorine to form hydrogen chloride (hydrochloric acid), and the oxygen is set free—

$$H_2O + Cl_2 = 2HCl + O.$$

In order to prepare oxygen by this reaction, chlorine gas is caused to bubble through water which is briskly boiling in a glass flask, F (Fig. 32). The mixture of chlorine and steam is then passed through a porcelain tube filled with fragments of porcelain, and maintained at a bright red heat in a furnace. The issuing gases are passed through a Woulf's bottle, containing a solution of sodium hydroxide, in order to absorb the hydrochloric acid, and the oxygen is collected at the pneumatic trough.

(13.) Oxygen is formed on a large scale in nature by the decomposition of atmospheric carbon dioxide by the green leaves of plants, under the influence of light. The carbon dioxide is decomposed into carbon, which is assimilated by the plant, and into oxygen which is thrown into the atmosphere. It has been estimated that 1 square metre of green leaf is able, under the influence of sunlight, to decompose more than 1 litre of carbon dioxide per hour.

(14.) Of the many other methods by which it has been proposed, from time to time, to manufacture oxygen on a large scale, may be mentioned one, known as the Tessié du Motay process, from the name of the inventor. This method consists in the alternate formation and decomposition of sodium manganate. The process consists of two operations, which are carried out at different temperatures. When a current of air is passed over a moderately heated mixture of manganese dioxide and sodium hydroxide, sodium manganate is formed—

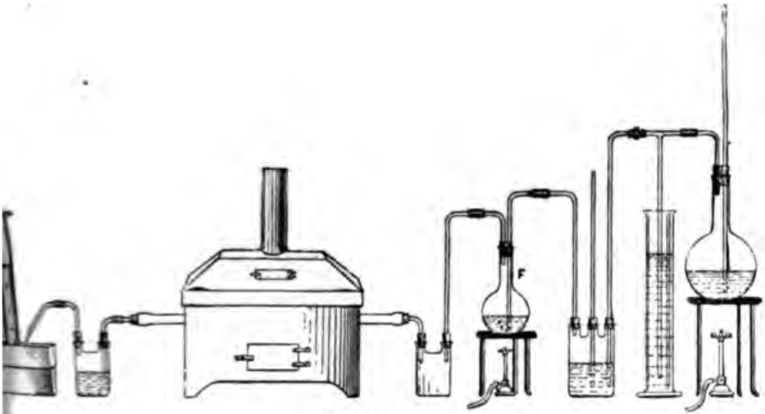

FIG. 32.

$$2MnO_2 + 4NaHO + O_2 = 2H_2O + 2Na_2MnO_4.$$

And if this sodium manganate be heated to bright redness, and a current of steam at the same time passed over it, the manganate is reduced to dimanganic trioxide, sodium hydroxide is reformed, and oxygen evolved, thus—

$$2Na_2MnO_4 + 2H_2O = Mn_2O_3 + 4NaHO + 3O.$$

On again passing air over the residue, after allowing the temperature of the mass to fall to that at which the first reaction was conducted, sodium manganate is once more reformed—

$$Mn_2O_3 + 4NaHO + 3O = 2H_2O + 2Na_2MnO_4.$$

**Properties.**—Oxygen is a colourless gas, having no taste or smell. It is slightly heavier than air, its specific gravity being 1.1056 (air = 1). One litre of the gas, at the standard temperature and pressure, weighs 1.43028 grammes. Oxygen is slightly soluble in water. 1 c.c. of water at 0° C. dissolves 0.0489 c.c. of oxygen measured at 0° C. and 760 mm. pressure. The solubility of oxygen in water, diminishes as the temperature rises in accordance with the interpolation formula (Winkler):—

$$c = 0.0489 - .0013413t + .0000283t^2 - .00000029534t^3.$$

Fish are dependent upon the dissolved oxygen in water for their supply of this gas for respiration. Oxygen is also soluble in molten silver, which is capable of absorbing about ten times its own volume of this gas (see Silver).

Oxygen is endowed with very powerful chemical affinities. Even at the ordinary temperature it is able to combine with such elements as phosphorus, sodium, potassium, and iron. All the chemical phenomena exhibited by the atmosphere, are due to the presence in it of free oxygen, the atmosphere being practically oxygen diluted with four times its volume of nitrogen. Thus, when a piece of bright metallic sodium is exposed to the air, the surface becomes instantly tarnished, and coated over with a film of oxide: when iron rusts, it in the same way is being acted upon by the oxygen of the air, forming oxide of iron: in these cases the metals are said to become *oxidised*. If the metal be obtained in a sufficiently finely divided condition before being exposed to the air, or to pure oxygen, this process of oxidation may proceed so rapidly, that the heat developed by the combination will cause the metal to burn. When the process of oxidation is accompanied by light and heat, the phenomenon is known as *combustion*, the oxygen being spoken of as the *supporter of combustion*: bodies which burn in the air, therefore, are simply undergoing rapid combination with oxygen. It will obviously follow, that bodies which are capable of burning in the air, will burn with greatly increased rapidity and brilliancy, when their combustion is carried on in pure or undiluted oxygen. A glowing chip of wood, or a taper with a spark still upon the spark, when plunged into pure oxygen, will be instantly rekindled. Such substances as sulphur, charcoal, phosphorus, which readily burn in air, when burnt in pure oxygen, carry on their combustion with greatly increased brilliancy. Many substances which are not usually regarded as combustible bodies will burn in oxygen, if their temperature be raised sufficiently high to initiate the combustion; thus a steel watch-spring, or a bundle of steel wires, if strongly heated at one end, will burn in oxygen, throwing out brilliant scintillations. This experiment is most readily shown by projecting a spirit-lamp flame upon the ends of a bundle of steel wire, by means of a stream of oxygen, as shown in Fig. 33. As soon as the ends of the wire are sufficiently heated, and begin to burn, the lamp may be withdrawn and the wire held in the issuing stream of oxygen, in which it will continue its combustion with great brilliancy.*

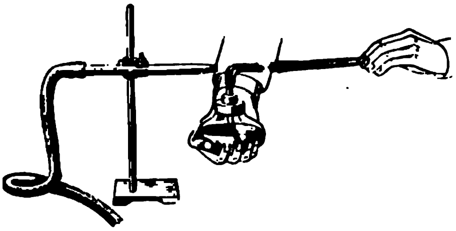

FIG. 33.

It is a remarkable fact, and one which has not yet received any satisfactory explanation, that these instances of combustion in oxygen will not take place if both the gas and the material be *absolutely* dry. It has been shown that phosphorus, sealed up in a tube with oxygen which has been absolutely freed from aqueous vapour, may even be distilled in the gas without any combination taking place. The presence of the minutest trace of moisture, however, is sufficient to allow the action to proceed, but the exact way in which this operates in causing the effect is at present not known with certainty. See also p. 12.

Oxygen is the only gas which is capable of supporting respiration: an animal placed in any gas or gaseous mixture containing no free oxygen rapidly dies. Undiluted oxygen may be breathed with impunity for a short time, but its continued inhalation soon produces febrile symptoms. The inhalation of oxygen is occasionally had recourse to in cases of asphyxiation, or under circumstances of great bodily prostration, where the necessary oxygenation of the blood cannot take place on account of the enfeebled action of the lungs.

---

* *See also Experiments 48 to 52,* "Chemical Lecture Experiments."

Compressed oxygen acts upon the animal economy as a poison: an animal placed in oxygen gas under a pressure of only a few atmospheres quickly dies.

During the respiration of man, air is drawn into the lungs, and is there deprived of 4 to 5 per cent. of its oxygen, and gains 3 to 4 per cent. of carbon dioxide. The oxygen that is withdrawn from the inhaled air by means of the lungs, is absorbed by the blood. The power to absorb this oxygen is believed to reside in a crystalline substance, contained in the corpuscles of the blood, called *hæmoglobin*, with which it enters into feeble chemical union, forming the substance known as *oxyhæmoglobin*. This substance is red, and imparts to arterial blood its well-known colour. During its circulation in the system, the oxyhæmoglobin parts with its oxygen, and is reconverted into the purple-coloured hæmoglobin. Under normal conditions, the whole of the oxyhæmoglobin is not so reduced, for venous blood is found still to contain it to some extent. The amount of carbon dioxide exhaled is diminished during sleep, and to a still greater extent during hibernation.

Oxygen can be liquefied at very low temperatures by the application of moderate pressure (see Liquefaction of Gases). It was first liquefied in 1877 by Cailletet, and independently by Pictet. Its critical temperature is −113°, at which point, a pressure of 50 atmospheres is required to bring about its liquefaction.

Liquid oxygen is a pale steel-blue, mobile liquid, which boils at −181°. Its specific gravity at −181° is 1.124. The liquid expands, when warmed, much more rapidly than gases do for the same increment of temperature, and its density diminishes in proportion, thus—

At −181° density = 1.124.
" −139° " = .877.
" −134° " = .806.
" −129° " = .755.

## ISOMERISM—POLYMERISM—ALLOTROPY.

**Isomerism.**—It is frequently found that two different compounds have the same composition; that is, their molecules are composed of the same number of the same atoms, and yet the substances have different properties. Such compounds are said to be *isomeric*, the one is an *isomer* of the other, and the phenomenon is called *isomerism*. Cases of isomerism are so numerous among the compounds of carbon (*i.e.*, in the realm of organic chemistry, see Carbon, p. 259), that it has been found convenient to classify them. The term isomerism, therefore, is frequently restricted to cases in which the compounds have the same percentage composition, the same molecular weight, and belong to the same chemical type or class of substances. Thus, the two compounds, dimethyl benzene and ethyl benzene, are both expressed by the formula $C_8H_{10}$. The molecules in each case contain 8 atoms of carbon and 10 atoms of hydrogen, they therefore have the same molecular weight and the same percentage composition; and as they both belong to the same type, or family, they are said to be isomeric with each other. The difference in the properties of these compounds is due to a difference in the arrangement of the atoms within the molecules, and this difference is expressed in their formulæ in the following manner:—

Dimethyl benzene, $C_6H_4(CH_3)_2$. Ethyl benzene, $C_6H_5(C_2H_5)$.

Different compounds having the same molecular weight and the same percentage composition, but which do not belong to the same family of compounds, are distinguished as *metamers*. Thus, the two compounds, acetone and allyl alcohol, are each expressed by the formula $C_3H_6O$. They have the same molecular weight and the same percentage composition, but belong to two widely different types of compounds; they are therefore called *metameric* compounds. The difference between them is again due to a difference in molecular structure, and they are distinguished by formulæ which convey this difference, thus:—

Acetone, $CO(CH_3)_2$. Allyl alcohol, $C_3H_5(HO)$.

**Polymerism.**—This term is employed to denote those cases in which different compounds belonging to the same family have the same percentage composition, but differ in molecular weight; that is to say, their molecules are composed of the same elements, which are present in the same *proportion*; but they do not contain the same actual numbers of the various atoms, and therefore have different weights. Thus, the compounds, ethylene, $C_2H_4$; propylene, $C_3H_6$; butylene, $C_4H_8$, belong to the same family, and have each the same percentage composition, but they differ in molecular weight. These substances are said to be polymers of one another.

**Allotropy** may be regarded as a special case of polymerism. In its widest sense the term is sometimes used to denote polymerism in general, but it is usually restricted to those instances of polymerism which are exhibited by elementary bodies only. Many of the elements are capable, under special conditions, of assuming such totally different habits and properties, that they appear to be entirely different substances. Thus, the element sulphur, as usually seen, is a primrose-yellow, opaque, solid substance, extremely brittle, and readily dissolved by carbon disulphide. Under certain circumstances it may be made to appear a totally different thing; it is then a translucent amber-coloured substance, soft and elastic like indiarubber, and insoluble in carbon disulphide; it is still sulphur, and sulphur only. Phosphorus, again, as usually known, is a nearly colourless, translucent, wax-like solid, which melts at a temperature only slightly above that of the hand, and which takes fire a few degrees higher; it is also extremely poisonous. Under special influences phosphorus can be made to assume the following properties:—A dark reddish-brown powder, resembling chocolate, which may be heated to 250° without taking fire, and which is non-poisonous. The substance is still phosphorus, and phosphorus only. This property possessed by certain of the elements of appearing in more than one form, of assuming, as it were, an *alias*, is called *allotropy*; the more uncommon form being spoken of as the *allotropic modification*, or the *allotrope* of the other.

From a study of the best known instances of this phenomenon, it is believed that allotropy, in all cases, is due to a difference in the number of atoms of the element that are contained in the molecule. In the case of ozone, which is the allotrope of oxygen, this is known to be the case. Ordinary oxygen molecules consist of two atoms, while the molecule of ozone is an aggregation of three oxygen atoms.

## OZONE.

Molecular symbol, $O_3$. Molecular weight, 47.88. Density, 23.94.

**History.**—When an electrical machine is in operation, a peculiar and characteristic smell is noticed in its vicinity. The same smell is sometimes observed in and about buildings, or other objects, when struck by lightning. In 1785 it was observed by Van Marum that when electric sparks were passed in oxygen, the oxygen acquired this peculiar smell. Schönbein (1840) showed that the oxygen obtained by the electrolysis of water, also contained this substance having a smell, and he gave to it the name *ozone*, signifying *a smell*. Schönbein made a careful study of the substance, and found that it might be obtained by various other methods. The more recent work of Andrews, Soret, and Brodie has brought our knowledge of the constitution of ozone to its present state.

**Occurrence.**—Ozone is present in the atmosphere in extremely small quantities (see Atmospheric Ozone).

**Modes of Formation.**—(1.) Mixed with an excess of oxygen, ozone is best obtained by exposing pure dry oxygen to the influence of the silent electric discharge. This may be effected by means of the instrument shown in Fig. 34, known as "Siemens' ozone tube."

consists of two concentric glass tubes, A and B. Tube A is coated on its *inner* surface with tinfoil, which is brought into metallic ntact with the binding screw D, as shown in the figure. Tube B coated upon the *outer* surface, also with tinfoil, which is in tallic connection with binding screw C. These two surfaces of foil are connected by means of their respective binding screws

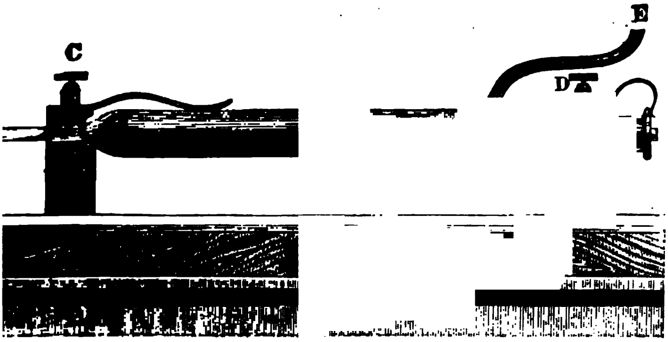

FIG. 34.

the terminals of a Ruhmkorf coil, and the slow stream of oxygen ich is admitted at E, and which passes along the annular space tween the two tubes, is there exposed to the action of the silent ctric discharge. A small portion of the oxygen so passing, comes converted into the allotropic modification, and the mixture

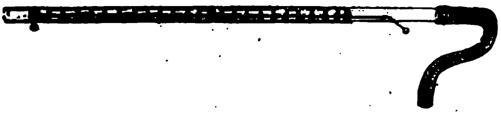

FIG. 35.

oxygen and ozone issues from the narrow tube at the opposite d of the apparatus.

For general purposes of illustration, a very simple arrangement y be substituted for the above. It consists, as shown in Fig. 35, a straight length of narrow glass tube having a piece of platinum re down the inside, which passes out through the walls of the e near to one end, and is there sealed to the glass. A second platinum wire is coiled round the outside of the tube, and these two wires are connected to the induction coil. On passing a slow stream of oxygen through the tube, the issuing gas will be found to be highly charged with ozone.

(2.) Ozone is also formed when an electric current is passed through water acidulated with sulphuric acid. Thus, in the ordinary electrolysis of water, the oxygen evolved from the positive electrode is found to contain ozone in sufficient quantity to be readily detected, both by its odour, and by other tests.

(3.) During many processes of slow oxidation at ordinary temperatures, ozone is formed in varying quantities. Thus, when phosphorus is exposed to the air, an appreciable amount of ozone is formed. One or two short sticks of freshly scraped phosphorus are for this purpose put into a stoppered bottle containing air, and allowed to remain for a short time, when the air will be found to contain ozone.

(4.) Ozone is also found during the combustion of ether upon the surface of red-hot platinum. When a spiral of platinum wire is warmed in a gas-flame, and while hot is suspended over a small quantity of ether contained in a beaker, the mixture of ether vapour and air undergoes combustion upon the surface of the platinum, which continues in an incandescent state so long as any ether remains. During this process of combustion, a considerable quantity of ozone is formed. (See also Peroxide of Hydrogen.)

(5.) Ozone is formed during the liberation of oxygen in a number of the reactions by which that gas is obtained; thus from manganese dioxide and sulphuric acid the oxygen that is evolved contains sufficient ozone to answer to the ordinary test. In the same way, by the action of sulphuric acid upon barium peroxide or potassium permanganate, this allotrope is present with the ordinary oxygen that is evolved.

**Properties.**—As prepared by any of the methods described, ozone is always mixed with a large excess of unaltered oxygen, probably never less than about 80 per cent. of the latter gas being present. Even in this state of dilution it has a strong and rather unpleasant smell, which rapidly induces headache. When inhaled it irritates the mucous membranes, and is rather suggestive of dilute chlorine.

Ozone is a most powerful oxidising substance; it attacks and rapidly destroys organic matter: on this account ozonised oxygen cannot be passed through the ordinary caoutchouc tubes, as these immediately destroyed by it. It bleaches vegetable colours, most metals are at once acted upon by it. Even metals like cury, which are entirely unaltered by ordinary oxygen, are cked by ozone. Its action upon mercury is so marked in its lt, that the presence of exceedingly small traces of ozone can be cted by it; the mercury is seen to lose its condition of perfect idity, and adheres to the surface of the glass vessel containing aving "tails" upon the glass. Ozone converts lead sulphide S) into lead sulphate ($PbSO_4$), and liberates iodine from potas- ı iodide—

$$2KI + H_2O + O_3 = O_2 + I_2 + 2KHO.$$

s property is generally made use of for detecting the presence sone, advantage being taken of the fact, that iodine, when set from combination in the presence of starch, gives rise to a p blue-coloured compound, the reaction being one of extreme cacy. In order to apply this test for ozone, strips of paper are ed in an emulsion of starch to which a small quantity of potas- n iodide has been added. These papers may be dried and served, and are usually spoken of as ozone test papers. When of these papers is moistened with water, and placed in air taining ozone, the iodine is liberated from the potassium iodide, being in the presence of starch, the paper instantly becomes by the formation of the coloured compound of starch. It will obvious that this method of testing for ozone can only be relied n, when there is no other substance present which is able to ompose potassium iodide; for example, when testing for ozone he atmosphere, the presence of oxides of nitrogen or peroxide hydrogen (both of which are capable of liberating iodine, and liable to be present in the air), would materially vitiate the lt (see also Atmospheric Ozone). The above decomposition otassium iodide by ozone, may be made use of as a test for ne in another way, which, although less delicate, is also less ly to be vitiated by the presence of other substances. Blue us papers are dipped into water which has been rendered very ly acid, and to which a small quantity of potassium iodide has n added. The papers may be dried and preserved. On stening one of these papers with water and exposing it to ne, the iodide is decomposed as in the former case, and the assium hydroxide which is formed, being a powerfully alkaline stance, converts the colour of the litmus from red to blue.

When heated to a temperature of about 250°, ozone is retransformed into ordinary oxygen; if, therefore, the ozonised gas obtained by means of the Siemens' ozone tube, be passed through a glass tube heated by means of a Bunsen flame, the whole of the ozone will be decomposed, and the issuing gas will therefore be found to be without action upon the ozone test papers.

Ozone is also decomposed by certain metallic oxides, such as those of manganese, copper, and silver. The action appears to be one of alternate reduction and oxidation, the metallic oxide remaining unaltered at the conclusion, thus—

$$Ag_2O + O_3 = Ag_2 + 2O_2,$$
$$Ag_2 + O_3 = Ag_2O + O_2.$$

The oxidising power of ozone is due to the instability of the molecule, and the readiness with which it loses an atom of oxygen, leaving a molecule of ordinary oxygen, thus—

$$O_3 = O + O_2.$$

The oxygen molecule is comparatively inert, but the liberated atom in its nascent state, is endowed with great chemical activity. No change of volume accompanies these processes of oxidation by ozone, as the volume of the oxygen molecule ($O_2$) is the same as that of the ozone molecule ($O_3$), the third atom of oxygen being that which enters into new combination with the oxidised substance.

Ozone is soluble to a slight extent in water, imparting to the solution its own peculiar smell. 1000 c.c. of water dissolve about 4.5 c.c. of ozone.

Under the influence of extreme cold, ozone condenses to liquid having an intense blue colour. So deep is the colour, that a layer of it 2 mm. in thickness is opaque. This liquid is obtained by passing ozonised oxygen through a tube which is cooled by being immersed in boiling liquid oxygen, which has a temperature of −181°. At this temperature the ozone liquefies, but the oxygen with which it was mixed passes on. Liquid ozone boils at −106. It is described by Olszweski and Dewer as an extremely explosive substance.

**Constitution of Ozone.**—The fundamental difference between ordinary oxygen and its allotrope ozone, lies in the fact that the molecule of the latter contains three atoms, while that of ordinary oxygen consists of only two. Ozone, therefore, is a polymer of oxygen; its molecule is more condensed, three atoms occupying two unit volumes. This conclusion as to the constitution of ozone has been arrived at from the consideration of a number of experimental facts.

(1.) When oxygen is subjected to the action of the electric discharge, it is found to undergo a diminution in volume.* This was shown by Andrews and Tait, by means of the tube seen in Fig. 36. The tube was filled with dry oxygen, which was prevented from escaping by means of the sulphuric acid contained in the bent portion of the narrow tube, which served as a manometer. When the silent discharge was passed through the oxygen, a contraction in the volume took place, indicated by a disturbance of the level of the acid in the syphon. When the tube was afterwards heated to about 300° C. and allowed to cool, the gas was found to have returned to its original volume, and to be devoid of ozone. This could be repeated indefinitely, the gas contracting when ozonised, and re-expanding when the ozone was converted by heat into ordinary oxygen. As only a very small proportion of the oxygen was converted into ozone, this experiment alone afforded no clue as to the relation between the change of volume and the extent to which this conversion took place.

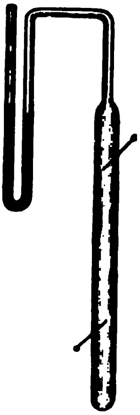
FIG. 36.

(2.) A small sealed glass bulb, containing a solution of potassium iodide, was placed in the tube before the experiment. The oxygen was ozonised, and the usual contraction noticed. The bulb was then broken, and on coming in contact with the ozone present, the potassium iodide was decomposed, iodine being liberated. No further contraction, however, followed; and, further, when the tube was subsequently heated to 300° and cooled, the gas suffered no increase in volume. By carefully estimating the amount of iodine that was liberated by the ozone, the actual amount of oxygen which had caused this liberation could be determined, according to the equation—

$$2KI + H_2O + O = I_2 + 2KHO,$$

---

* "Chemical Lecture Experiments," No. 63.

and it was found, that the volume of oxygen so used up, was exactly equal to the contraction which first resulted on the ozonisation of the oxygen.

These facts proved that when potassium iodide was oxidised by ozone, a certain volume of ordinary oxygen was liberated, which was equal to the volume of ozone; and a certain volume was used up, which was equal to the original contraction.

These facts were explained by the supposition, that ozone was represented by the molecular symbol $O_3$; and its action upon potassium iodide may be expressed as follows—

$$2KI + H_2O + O_3 = O_2 + I_2 + 2KHO.$$

(3.) To prove the correctness of this supposition, however, it was necessary to learn the exact relation between these two volumes. This Soret did, by making use of the property possessed by turpentine (and other essential oils) of absorbing ozone without decomposing it; and he found, that the diminution in volume which took place, by absorbing ozone from ozonised oxygen, was exactly twice as great as the increase in volume that resulted when the same volume of ozonised oxygen was heated.

(4.) If the molecule of ozone be correctly represented by $O_3$, its density will be 24, as against 16 for oxygen; and its rate of diffusion will be proportionately slower in accordance with the law of gaseous diffusion (see Diffusion of Gases, p. 81). Soret found that this was actually the case, and from his experiments the number 24 for the density of ozone receives conclusive confirmation.

# CHAPTER III

## *COMPOUNDS OF HYDROGEN WITH OXYGEN*

THERE are two oxides of hydrogen known, viz.:—

| | |
|---|---|
| Hydrogen monoxide, or water . . . . . | $H_2O$ |
| Hydrogen dioxide . . . . . . . . | $H_2O_2$ |

### WATER.

Formula, $H_2O$. Molecular weight = 17.96.

Until the time of Cavendish, water was considered to be an elementary substance. Priestley had noticed that when hydrogen and oxygen were mixed and inflamed, moisture was produced, and he had also observed that the water so obtained was sometimes acid. Cavendish showed, that the water was actually the product of the chemical union of hydrogen with oxygen, and he also discovered that the acidity which this water sometimes possessed, was due to the presence of small quantities of nitric acid; and he traced the formation of this acid to the accidental presence of nitrogen (from the atmosphere) with which the gases were sometimes contaminated.

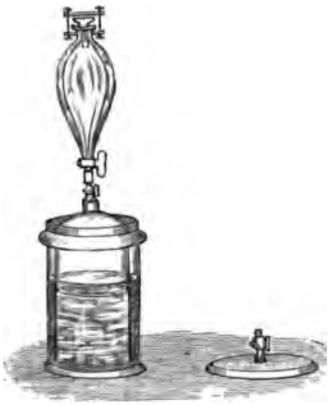

FIG. 37.

Cavendish filled a graduated bell-jar with a mixture of hydrogen and oxygen, in the proportion of two volumes of the former to one of oxygen, and he attached to the bell-jar a stout glass vessel, resembling the pear-shaped apparatus shown in Fig. 37, *which was perfectly* dry, and rendered vacuous. On opening the stop-cocks, gas entered the exhausted tube, which is furnished at the top with two platinum wires. The cocks were again closed and an electric spark passed through the mixed gases, thereby causing their explosion, when the interior surface of the previously dry glass vessel was found to be dimmed with a film of moisture. On again opening the stop-cocks, more gas was drawn into the upper vessel, the same volume passing in as originally entered the evacuated apparatus. This showed that the two gases in their combination with each other had entirely disappeared. By repeatedly filling the vessel with the mixed gases, and causing them to unite in this way, Cavendish succeeded in collecting sufficient of the water to identify the liquid, and prove that it was in reality pure water.

The more exact volumetric proportion in which oxygen and hydrogen combine to form water, has been determined by modern eudiometric methods, which have been developed from Cavendish's experiment. Accurately measured volumes of the two gases are introduced into a long graduated glass tube, standing in the mercurial trough, and provided with two platinum wires, by means of which an electric spark can be passed. The gases are caused to unite by means of the spark, and the contraction in volume is carefully observed. Fig. 38 shows the apparatus for this purpose. The long glass tube A having a millimetre scale graduated upon it, and having two platinum wires sealed into the glass near the upper and closed end, is completely filled with mercury, and inverted in the trough of the same liquid : this tube is known as a eudiometer. A quantity of pure oxygen is then introduced into the tube, and the volume occupied by the gas carefully read off upon the graduations. Seeing that the volume occupied by a given mass of gas is dependent both upon the temperature and the pressure, each of these factors has to be taken into account in the process of this experiment. The temperature is ascertained by the attached thermometer T. The pressure under which the gas is, will be the atmospheric pressure at the time (ascertained by the barometer B placed near the apparatus) *minus* the pressure of a column of mercury, equal to the height of the mercury within the eudiometer above the level of that in the trough. This height is obtained in millimetres, by carefully reading upon the graduated scale the level of the mercury in the trough, and the top of the column in the tube, and the number of millimetres so obtained is deducted from the barometric reading. These observations are made by means of a telescope placed at such a convenient distance, that the heat of the body may not introduce disturbances.

The data obtained, give the volume of gas at a particular temperature, and under a pressure less than that of the atmosphere. By the process of calculation explained under the general properties of gases (p. 69), this is reduced to the standard temperature and pressure, viz., 0° and 760 mm.

A quantity of hydrogen is then introduced into the eudiometer, considerably in excess of that required for complete combination with the oxygen, and the volume again ascertained with the above precautions and corrections.

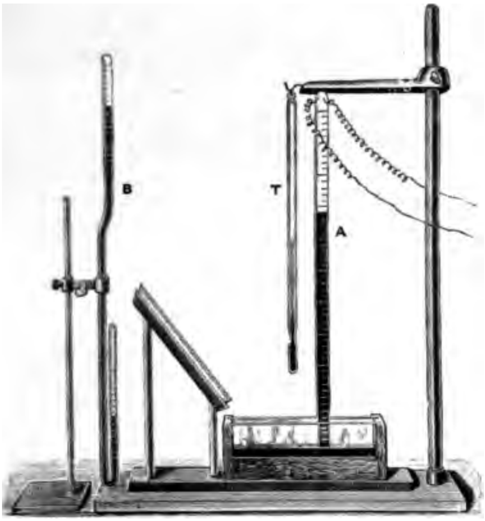

FIG. 38.

The difference between the first and second reading will give the volume of hydrogen which has been added.

The eudiometer is then firmly held down against a pad of caoutchouc upon the bottom of the trough, and the gases fired by an electric spark from a Ruhmkorff coil. A bright flash of light passes down the tube, and on releasing it from the indiarubber bed, mercury enters to fill the space previously occupied by the gases which have combined.

On allowing the instrument to once more acquire the temperature of the surrounding atmosphere, the residual volume is read off, and corrected for temperature and pressure.

The following data have now been obtained :—

(1.) The volume of oxygen, corrected for temperature and pressure.

(2.) The volume of mixed oxygen and hydrogen, corrected for temperature and pressure.

(3.) The volume of residual hydrogen, corrected for temperature and pressure.

A concrete example will explain how the result is deduced from these observations :—

| | |
|---|---|
| Corrected volume of oxygen used . . . . . . | 45.35 |
| Corrected volume after the addition of hydrogen . . | 256.05 |
| Corrected volume of residual hydrogen . . . . | 120.10 |

$256.05 - 45.35 = 210.70$ = total volume of hydrogen employed.

$210.70 - 120.10 = 90.60$ = volume of hydrogen which has combined with 45.35 volumes of oxygen.

$$\therefore 43.35 : 1 :: 90.60 : 1.997.$$

$\therefore$ One volume of oxygen has combined with 1.997 volumes of hydrogen to form water.*

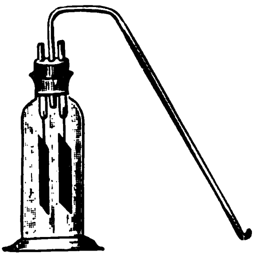

FIG. 39.

The volume composition of water may be shown by analytical processes, as well as the synthetical method described above. This decomposition of water is most conveniently effected by means of an electric current. If the two terminals from a galvanic battery are connected to two pieces of platinum wire or foil, and these are dipped into acidulated water, bubbles of gas make their appearance upon each of the wires. If these two strips of platinum be so arranged in a bottle, that all the gas evolved escapes by a delivery-tube (Fig. 39), it will be found that the gas explodes violently on the application to it ıted taper, showing it to be a mixture of oxygen and hy·

---

* In accurate experiments the volume occupied by the minute quantity of water formed, has to be taken into account, and a number of other corrections have to be made that are not mentioned in this outline description of the process.

By modifying the apparatus in way that the gas from each ı plate shall be collected in sepaes, so arranged that the volumes ases can be measured, it is found ce as much hydrogen is evolved, ven time, as oxygen. A converm of voltameter is seen in Fig. re the two measuring tubes are ed over the platinum plates conn a glass basin. The electrode, s connected with the negative l of the battery, is the one from the larger volume of gas, viz., rogen, is evolved, while the oxyberated at the positive plate.

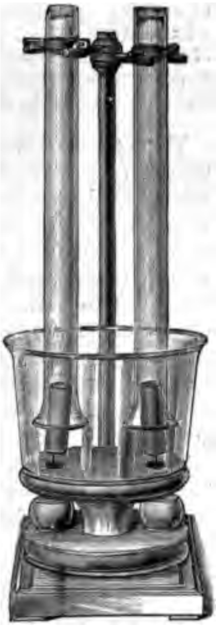

FIG. 40.

ı the volumes of the gases are measured, it is found that they exactly in the proportion of two ogen to one of oxygen, but that gen is in deficit of this propor- This is due, in the first place, greater solubility of oxygen in han of hydrogen; and, secondly, formation of a certain quantity of luring the electrolysis, whereby a shrinking of volume in the proportion of three to two.

electrolysis of water," as this process is usually called, is not the henomenon that at first sight it might appear to be. In the first re water is not an electrolyte, and it is necessary either to acidulate ender it alkaline by the addition of sodium or potassium hydroxides. action of the electric current is (in the case of water acidulated with acid) to decompose the sulphuric acid into $H_2$, which appears at the electrode, and $SO_4$, which is liberated at the anode. $SO_4$, however, wn into $SO_3 + O$, the oxygen being liberated, and the sulphur trioxide niting with a molecule of water present, to regenerate sulphuric acid. ges may be thus represented :—

$$\begin{array}{lcll} & & \text{At the Cathode.} & \text{At the Anode.} \\ H_2SO_4 & = & H_2 \; + & (SO_3 + O). \\ SO_3 + H_2O & = & H_2SO_4. & \end{array}$$

tly, therefore, the water is decomposed. As already stated, some of the nascent oxygen is converted into ozone, some also unites with water to form hydrogen peroxide, $H_2O_2$, and probably a still larger quantity is employed in oxidising the sulphuric acid to persulphuric, which is always formed in solution at the anode. Berthelot considers that the variation of the proportion of hydrogen and oxygen evolved during the electrolysis of dilute sulphuric acid, from the proportion of two volumes of hydrogen to one volume of oxygen, is mainly, if not entirely, due to the formation of persulphuric acid.

**The Volumetric Composition of Steam.**—When a mixture of oxygen and hydrogen is exploded in a eudiometer, we have seen that a certain contraction of volume follows, due to the formation of water by the uniting gases. The oxygen and hydrogen that have entered into combination have disappeared as gases, the volume of the resultant water being practically negligable. It is important to know what relation exists between the volume of the uniting gases, and the volume of the product of their combination when in a state of vapour; that is to say, what volume of steam is produced by the union of one volume of oxygen with two volumes of hydrogen; in other words, whether there is any molecular contraction in the formation of steam.

To ascertain this, the mixed gases, in the exact proportions to form water, must be made to combine under such circumstances that the product shall remain in a state of gas or vapour, so that its volume, and that of the mixed gases, may be measured under comparable conditions. For this purpose a mixture of oxygen and hydrogen, obtained by the electrolysis of acidulated water, is introduced into the closed limb of the U-shaped eudiometer shown in Fig. 41.* This tube is graduated into three equal divisions, indicated by the broad black bands, and is furnished with two platinum wires at the closed end. It is also surrounded by an outer tube, so that a stream of vapour from some liquid, boiling above the boiling-point of water, can be made to circulate. The most convenient liquid for the purpose is amyl alcohol, which boils at 130° In this way the eudiometer, and the contained gases, will be maintained at a constant temperature, high enough to keep the water formed by their combination, in the state of vapour.

The amyl alcohol is briskly boiled in the flask, and its vapour is led into the tube surrounding the eudiometer. The temperature of the mixed gases is thereby raised to 130°, and they occupy the three divisions of the tube when the mercury in the open limb is at the same level, that is, when the gases are under atmospheric pressure. The amyl alcohol vapour leaves the apparatus by the glass tube at the bottom, and is conveyed away and condensed. An electric spark is then passed through the gases by means of the induction coil. (In order to prevent the mercury from being forcibly ejected from the open limb of the U-tube at the moment of explosion, an additional quantity of mercury is poured in, and the open end is closed by the thumb when the spark is passed.) On bringing the enclosed gas again to the atmospheric pressure, by adjusting the level of the mercury until it is once more at the same height in each limb, it will be found that the mercury in the eudiometer is now standing at the second band; that is to say, the three volumes of gas originally present have now become two volumes of steam. This condensation is expressed in the molecular equation—

---

* See Experiments Nos. 72 and 73, "Chemical Lecture Experiments."

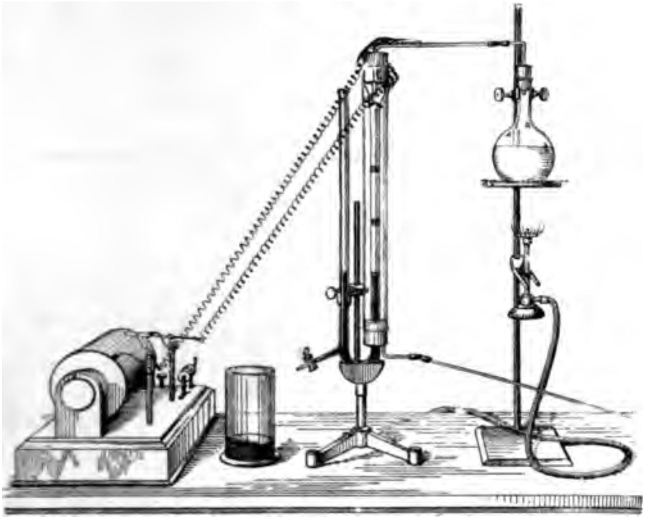

FIG. 41.

$$O_2 + 2H_2 = 2H_2O.$$

**The Gravimetric Composition of Water.**—Having learned the *composition of water by volume*, and knowing also that the relative weights of equal volumes of oxygen and hydrogen are as 15.95 : 2, the composition by weight can readily be calculated, thus—

| | |
|---|---|
| 1 volume of oxygen = | 15.96 |
| 2 volumes of hydrogen = | 2.00 |
| | 17.96 |

17.96 parts by weight of water are composed of 2.00 parts by weight of hydrogen, and 15.96 parts of oxygen, or, expressed centesimally, we have—

| | |
|---|---|
| Oxygen . . . . | 88.86 |
| Hydrogen . . . | 11.14 |
| | 100.00 |

The composition of water by weight has been experimentally determined with great care by a number of chemists.

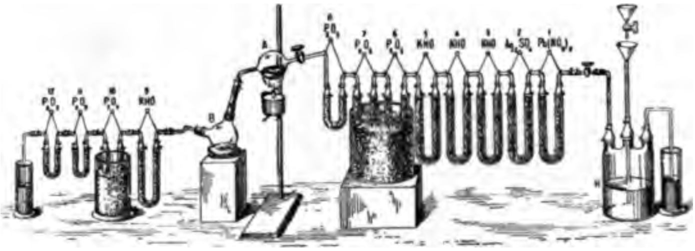

FIG. 42.

The apparatus shown in Fig. 42 represents the method employed by Dumas (1843). When copper oxide is heated in a stream of hydrogen, the copper oxide is deprived of its oxygen, which unites with the hydrogen to form water—

$$CuO + H_2 = Cu + H_2O.$$

Dumas' method is based upon this reaction. A weighed quantity of perfectly dry copper oxide was heated in the bulb A, in a current of hydrogen generated from zinc and sulphuric acid in the bottle H, and rendered absolutely pure and dry by its passage through a

›f tubes containing absorbents. The water formed by the ›f the hydrogen with the oxygen of the copper oxide, was ›d in the second bulb, B, previously weighed; and the un-›sed aqueous vapour which was carried forward in the stream ogen, was arrested in the weighed tubes which follow. The ; in weight of the bulb B and the weighed tubes, gave the ›ight of water produced; while the loss of weight suffered ›opper oxide, gave the weight of oxygen contained in that The difference between these two weights is the weight ydrogen that entered into combination with the oxygen. mean of many experiments it was found that in the forma- 236.36 grammes of water, the oxygen given up by the oxide was 210.04 grammes.

$$236.36 - 210.04 = 26.32,$$

e 236.36 grammes of water were made up of

$$\begin{array}{lr} \text{Hydrogen} = & 26.32 \\ \text{Oxygen} \ \ = & 210.04 \\ \hline & 236.36 \end{array}$$

io of hydrogen to oxygen is therefore as 2 : 15.96.

gen prepared from zinc and sulphuric acid is liable to contain traces of ılphuretted hydrogen. This is absorbed in the first tube containing broken glass moistened with a solution of lead nitrate.

rsenuretted hydrogen / hosphoretted hydrogen } absorbed in the second tube, filled with glass moistened with silver sulphate.

ılphur dioxide / arbon dioxide } absorbed in the third tube, containing in one limb pumice moistened with a solution of potassium hydroxide, and in the other fragments of solid potassium hydroxide.

; 4, 5, 6, and 7, containing solid potassium hydroxide and phosphorus le (the two latter being placed in a freezing mixture), are for the pur-›ithdrawing every trace of aqueous vapour. Tube 8 was weighed before r the experiment, in order to test the absolute dryness of the hydrogen ›red the bulb. In order to get rid of dissolved air, the dilute sulphuric d was previously boiled. Tubes 9, 10, 11 were weighed both before and : experiment; while tube 12, which was not weighed, was placed at the revent any absorption of atmospheric moisture by the weighed tubes.

the time of Dumas this subject has been reinvestigated by other enters, who have introduced various modifications into the process; ›h a view to finding the weight of hydrogen directly, and of eliminating the possible sources of error arising from the presence of impurities in the hydrogen, the hydrogen has been absorbed by palladium. The metal so charged with hydrogen, can be weighed before and after the experiment, and the actual *weight* of hydrogen used, directly ascertained.

Most recently the matter has been investigated by Scott and Rayleigh, and the results obtained show only the slightest departure from the numbers obtained by Dumas.

**Properties of Water.**—Pure water is a tasteless and odourless liquid. When seen in moderate quantities it appears to be colourless, but when viewed through a stratum of considerable thickness

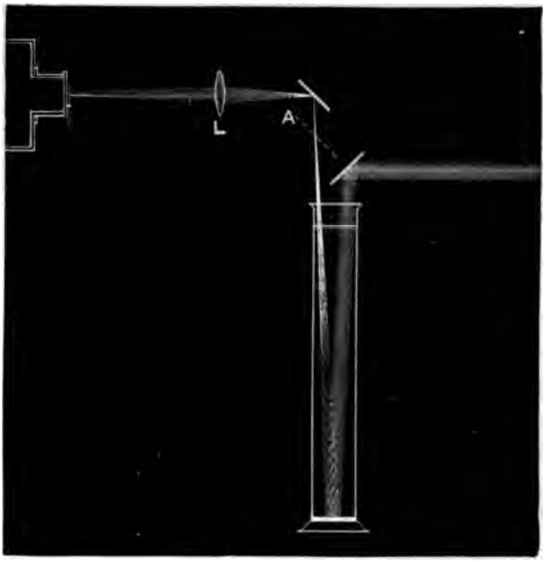

FIG. 43.

it presents a beautiful greenish-blue colour. This colour may be seen by filling a horizontal tube about 15 feet long with the purest water, and passing a strong beam of light through it. It may also be perceived by directing a ray of light through a tall cylinder of water in the manner shown in the figure, and causing it to be reflected up through the water from the surface of a layer of mercury at the bottom; the immerging ray, being then reflected upon a screen, shows the characteristic colour of the water. By intercepting the ay by a hand mirror at A, the white light can be thrown upon the creen, as a contrast to the greenish-blue tint.

Aitkin has recently shown, that the presence of extremely finely ivided suspended matters in water will give to the liquid the appearnce of a blue colour. Thus, in tanks where water is being softened y the addition of milk of lime, after the bulk of the precipitated chalk as settled, and only the finest particles still remain suspended in he liquid, it is often noticed that the water appears to have a rich lue colour. The wonderful blue colour of the waters of many of he Swiss lakes is probably due in part to this optical phenomenon, s well as to the intrinsic colour of the water. When a mass of ure snow, such as falls in high mountainous regions, is broken pen in such a way that the light is reflected from side to side of he small crevice, the true greenish-blue colour of the water is very nanifest.

**Water is compressible** to only a very slight extent; thus, under n additional pressure of one atmosphere, 1000 volumes of water ecome 999.95 volumes.

Small as this compressibility is, it exerts an important influence upon the istribution of land and water upon the earth. It has been calculated, that wing to this compression, where the ocean has a depth of six miles, its surface s lower by 620 feet than it would be if water were absolutely non-compressible; nd calculated from the average depth of the sea, its average level is depressed 16 feet. The effect of this depression of the sea-level is that 2,000,000 square niles of land are now uncovered, which would otherwise be submerged beneath he ocean.

**Water is an extremely bad conductor of heat.** A quantity of water ontained in a tube held obliquely, may be boiled by the application f heat to the upper layers, without appreciably affecting the emperature of the water at the bottom; a fragment of weighted ce sunk to the bottom will remain for a long time unmelted, while he water a few inches above it is vigorously boiling. This low onductivity for heat is shared in common by all liquids that are ot metallic. Indeed, Guthrie has shown, that water conducts heat etter than any other substance which is liquid at the ordinary emperature, with the exception of mercury.

**Steam.**—Under a pressure of 760 mm., water boils at 100° see p. 112), and is converted into a colourless and invisible gas, r vapour. The visible effect that is observed when steam is llowed to issue into the atmosphere, is due to the condensation of the steam in the form of minute drops of water. What is popularly called steam is in reality, therefore, not steam, but an aggregation of small particles of liquid water. The invisibility of steam is readily demonstrated by boiling a small quantity of water in a capacious flask; as the steam issues from the neck it condenses in contact with the cool air and presents the familiar appearance, but within the flask it will be perfectly transparent and invisible.

**Ice.**—At a temperature of 0° water solidifies to a transparent crystalline mass. In the act of solidification, the water expands by nearly $\frac{1}{10}$th of its volume, 10 volumes of water become 10.908 volumes of ice: solid water, therefore, is specifically lighter than liquid water, and floats upon its surface. Water in this respect is anomalous, for in the case of most other substances, the solid form is denser than the liquid. The disruptive force exerted by water at the moment of freezing, is the cause of the bursting of pipes and other vessels containing water during winter; and it is also an important factor in the economy of nature, in the disintegration of rocks and of soil. Under certain conditions, water may be cooled many degrees below 0° without solidification taking place. Thus, if a small quantity of water contained in a vacuous tube be carefully cooled without being subjected to vibration, its temperature may be lowered to − 15° without it solidifying; a slight shock, however, at once causes it to pass into the solid state, when its temperature instantly rises to 0° (see p. 118). Although the exact temperature at which water freezes is liable to uncertainty from this cause, the point at which ice melts is, under ordinary circumstances, constant, viz., 0°. Under increased pressure ice will melt at temperatures below 0°; thus Mousson found that, under a pressure of 13,000 atmospheres, ice melted at − 18°. The melting-point of ice is lowered by about 0.0074° by each additional atmosphere of pressure (see p. 119).

Between the temperatures of +4° and 100°, water follows the ordinary laws that govern the expansion and contraction of liquids due to change of temperature; if water be cooled from 100°, it gradually contracts until the temperature reaches 4°. Between this point and 0° it forms a remarkable exception to the general law, for, when cooled below 4°, it slowly expands instead of contracting, and continues expanding until 0° is reached, when it solidifies. At 4°, therefore, water expands whether it be heated or cooled; consequently, at this point it is denser than at any other temperature. This temperature is known as its point of maximum density. (The most accurate observations fix the exact point at 3.945°.)

The following table shows the change of volume suffered by water on being heated from 0° to 8°:—

| | | | |
|---|---|---|---|
| 1.000000 | volumes at | 0° | becomes |
| 0.999915 | „ | +2° | „ |
| 0.999870 | „ | 4° | „ |
| 0.999900 | „ | 6° | „ |
| 1.000000 | „ | 8° | |

One cubic centimetre of water, measured at its point of maximum density and at 760 mm., is the unit of weight of the metrical system, and is called a *gramme*.

It is also at this temperature, that water is taken as the unit for comparison of the densities of other liquids and of solids; thus, when it is stated that the density, or specific gravity, of diamond is 3.5, it is meant that diamond is 3.5 times as heavy as an equal bulk of water measured at its point of maximum density.

The fact that water has a point of maximum density remote from its freezing-point, is one of far-reaching consequences in the operations of nature.

When a mass of water, such as a lake, is exposed to the influence of a cold wind, the superficial layer of water is cooled, and thereby becoming specifically denser, it sinks to the bottom and exposes a fresh surface. This in its turn has its temperature lowered, and in like manner falls to the bottom. A circulation of the water in this way is set up, until the entire mass reaches a temperature of 4°. At this point the further cooling of the surface-layer causes expansion instead of contraction, and the colder water becoming specifically lighter now floats upon the top, where it remains until it congeals. If water continued to contract as its temperature was reduced below 4°, the circulatory motion would continue until the whole body of the water was cooled to 0°, when solidification of the entire mass would take place. The reason that certain very deep waters seldom or never freeze, is because the duration of the cold is not long enough to bring the temperature of the entire mass of the water down to 4°, and until that is effected, no ice can form upon the surface.

**The Solvent Power of Water.**—Water is possessed of more general solvent powers than any other liquid; that is to say, a larger number of substances are dissolved by water than by any other liquid. The solvent action of water upon gases, liquids, and solids, in so far as it is shared by other liquids, has been dealt with under the General Properties of Liquids (Part I., chap. xiii.).

**Water of Crystallisation.**—When solid substances are dissolved in water, and the water afterwards evaporated, the dissolved substance is frequently deposited in definite crystalline shapes. Many salts owe their crystalline nature to the fact, that a certain number of molecules of water have solidified along with molecules of the salt, each molecule of the salt being associated with a definite number of molecules of solid water. The water molecules must be regarded as having entered into a feeble chemical union with the salt molecule, but a union which is of a somewhat different order from that which holds together the atoms of oxygen and hydrogen in the water molecules, or the atoms composing the salt in the salt molecule (see p. 65). Thus, copper sulphate crystallises associated with five molecules of water, $CuSO_4,5H_2O$; magnesium sulphate with seven, $MgSO_4,7H_2O$. Water so associated with crystals is known as *water of crystallisation*, and the compound is called a *hydrate*.

Many salts are capable of crystallising with more than one definite number of molecules of water, depending upon the temperature at which the crystallisation takes place: thus sodium carbonate, crystallised at the ordinary temperature, has the composition, $Na_2CO_3,10H_2O$; while at temperatures between 30° and 50° the salt that is deposited contains 7 molecules of water, $Na_2CO_3,7H_2O$. Sodium chloride, crystallised from solution at $-7°$, has the composition, $NaCl,2H_2O$; while the crystals that are deposited at $-23°$ contain 10 molecules of water, $NaCl,10H_2O$.

In such cases as these, the particular crystalline form of the salt differs with the different degrees of hydration. Salts containing water of crystallisation, which are deposited from solution at temperatures below 0°, are sometimes termed *cryohydrates*.

Many crystalline salts, when exposed to the air, lose either some or all of their water of crystallisation, and in so doing, lose their particular geometric form. Thus, the salt, $Na_2CO_3,10H_2O$ (ordinary washing soda), when freely exposed, gradually loses its crystalline form and falls down to a soft white powder, which consists of small crystals of another form, having the composition $Na_2CO_3,H_2O$. *This process* is known as *efflorescence*, the crystals being said to *ffloresce.* Other crystals undergo exactly the reverse change; they combine with moisture from the air, and pass into other crystalline forms containing more water of crystallisation, or in some cases they absorb sufficient moisture to cause them to liquefy. Such substances are said to *deliquesce.* This property of certain salts, is made use of for withdrawing traces of water from either liquids or gases. Thus, such a liquid as ether may be freed from dissolved water, by adding to it copper sulphate containing one molecule of water of crystallisation, $CuSO_4,H_2O$ ; this compound takes up water and passes into $CuSO_4,5H_2O$, and thereby has the effect of drying the ether. Gases in the same way are frequently dried by being passed through tubes containing calcium chloride from which the water of crystallisation has been removed. This substance absorbs water with avidity, passing into the hydrated salt $CaCl_2,6H_2O$.

The characteristic colours of certain salts are in many cases dependent upon the amount of water of crystallisation they contain. Thus cobalt chloride, $CoCl_2,6H_2O$, is a pink salt. If it be gently heated to 120° it loses its water, and becomes $CoCl_2$, which has a rich blue colour. Solutions of this salt have been employed for the so-called *sympathetic inks.* The faint colour of the pink salt renders words written upon paper with its dilute solution practically invisible; but on warming the paper, and thereby expelling the water from the salt, the written characters appear in a blue colour, which again disappears as the salt is allowed to rehydrate itself by exposure to the air.

One of the most striking examples of this change of colour resulting from varying proportions of water of crystallisation, is seen in the salt magnesium platino-cyanide, which crystallises under ordinary circumstances as a bright scarlet salt with seven molecules of water, $MgPt(CN)_4,7H_2O$. When this salt is heated to about 50° it loses two molecules of water, and is converted into a canary-yellow salt, $MgPt(CN)_4,5H_2O$. If the temperature be raised to 100° the yellow salt becomes white by the loss of four more molecules, the composition of the white salt being $MgPt(CN)_4,2H_2O$. When a solution of the salt is carefully evaporated to dryness in a dish and gently warmed, these colour changes will be rendered evident; and upon exposing the dried and white residue to the air, or by gently breathing into the dish, the salt rehydrates itself, and is converted into the crimson compound having seven molecules of water.

Many salts can have their combined water withdrawn by powerful dehydrating agents; thus, if a crystal of copper sulphate ("blue vitriol," $CuSO_4,5H_2O$) be immersed in strong sulphuric acid, the acid abstracts four out of the five molecules from the salt, leaving the nearly white salt $CuSO_4,H_2O$; or when alcohol is added to a solution of cobalt chloride, or to crystals of the salt, $CoCl_2,6H_2O$, the alcohol abstracts water, and the solution becomes blue.

When salts containing water of crystallisation are heated, it frequently happens that a portion of the water is more easily parted with than the remainder. Thus copper sulphate, $CuSO_4,5H_2O$, when heated to 100°, parts with four molecules of water, leaving the salt $CuSO_4,H_2O$; and in order to drive off this one remaining molecule, the temperature must be raised above 200°. Zinc sulphate (or white vitriol), $ZnSO_4,7H_2O$, in like manner loses six molecules of water at 100°, but retains the seventh until a temperature of 240° is reached. In order, therefore, to distinguish between the water that is more firmly held and that which is readily parted with, the term *water of constitution* is frequently applied to the former, and the fact is sometimes expressed in notation in the following manner:—

$$CuSO_4H_2O,4H_2O\ ; \qquad ZnSO_4H_2O,6H_2O.$$

**Natural Waters.**—On account of the great solvent powers of water, this compound is never found upon the earth in a state of absolute purity; even rain, as it falls in regions far removed from the dirty atmosphere of towns, not only dissolves the gases of the atmosphere, but also small quantities of those suspended matters which are always present in the air. As soon as the rain reaches the earth, the water at once exerts its solvent action upon the mineral matter constituting the portion of the earth's crust over which it flows, and through which it percolates, and the liquid is rapidly rendered less and less pure as it travels on its course to lake or ocean.

Natural waters may be broadly divided into two classes, based upon the amount of dissolved impurities they contain. If the substances in solution are present in excessive quantities, or to such an extent as to be perceptible to the taste, the water is said to be a *mineral water;* while, on the other hand, waters that are not so rich in dissolved impurities are known as *fresh waters.*

**Mineral Waters.**—The most exaggerated examples of mineral waters are to be found in sea water, and in the waters of certain lakes, which, having no outlet, are fulfilling the purpose of enormous evaporating basins, in which the waters that flow into them are undergoing evaporation and therefore concentration; such, for example, as the salt lakes of Egypt, the Elton lake in Russia, and the Dead Sea. In waters of this description the total quantity of dissolved solid matter is very considerable, and, as in the case of the Dead Sea, is often deposited in crystalline masses round the shores of the lake. The following table gives the total amount of dissolved saline matter contained in 1000 grammes of certain of these waters:—

| | |
|---|---|
| Irish Sea | 33.86 |
| Mediterranean Sea | 40.0 |
| Dead Sea | 228.57 |
| Elton Lake | 271.43 |

As a typical example of a sea water, the composition of the water of the British Channel may be quoted; 1000 grammes of this water contain—

| | | |
|---|---|---|
| Sodium chloride | 27.059 | |
| Magnesium chloride | 3.666 | |
| Magnesium sulphate | 2.296 | |
| Calcium sulphate | 1.406 | |
| Potassium chloride | 0.766 | |
| Calcium carbonate | 0.033 | |
| Magnesium bromide | 0.029 | |
| | | 35.255 |
| Water | | 964.745 |
| | | 1000.000 |

Passing from these highly concentrated mineral waters, we find a large number of spring waters which are classed as *mineral*, not because the total quantity of foreign matter in solution is excessive, but rather because they contain an abnormally large proportion of a few special substances. Thus, large quantities of magnesium sulphate, and chloride, are found in such springs as those at Epsom and Friedrichshall. Others are found to contain considerable quantities of sodium sulphate and sodium carbonate; while those known as *chalybeate* waters, contain ferrous carbonate in solution. Spring waters that are charged with unusual quantities of soluble gases, are likewise placed in the category of mineral waters, such as the waters of Apollinaris and Seltzer, containing large quantities of carbon dioxide; and the sulphur springs at Harrogate and Aachen, which hold in solution sulphuretted hydrogen as well as alkaline sulphides.

**Fresh Waters.**—The purest form of natural water is rain water. The average weight of solid matter dissolved in rain water, collected in the country and in perfectly clean vessels upon which it exerts no solvent action, is found to be 0.0295 parts in 1000 parts of water. Collected in or near towns, rain water always contains a larger amount of dissolved impurities, such as nitrates, sulphates, ammoniacal salts, and often considerable quantities of sulphuric acid: it is the acid nature of the rain that causes so much damage to stone buildings.

The nature and extent of the contamination that rain water suffers after it has fallen, must obviously depend very largely upon geographical and geological circumstances, and therefore there are no special features that are distinctly characteristic of waters from rivers, lakes, or springs.

Thus, the total solid impurity in 1000 parts of water from the river Dee at Aberdeen is 0.057, while that contained in the Thames is 0.30 parts.

The water of Loch Katrine only contains 0.032 parts of solid matter dissolved in 1000 parts, while that of Elton lake contains as much as 271.43.

The same wide differences are also seen in spring waters from different geological strata. Spring waters from granite and gneiss rocks, contain on an average 0.059 parts of dissolved solid matter in 1000 parts, while those from magnesian limestone average as much as 0.665 parts. As a broad general rule, river waters are found to contain less solid matter in solution than spring waters, and these in their turn less than deep well waters. Thus, comparing waters from different sources, and selecting only such samples as are known to be free from pollution from either sewage matter or other abnormal impurities, it will be seen that, with regard to the dissolved solid matter they contain, they fall in the following order—

*Total Solid Impurity Dissolved in* 1000 *Parts of Unpolluted Waters.*

| | |
|---|---|
| Rain water (average of 39 samples) . . | .0295 |
| Rivers and lakes (average of 195 samples) . | .0967 |
| Spring waters (average of 198 samples) . . | .2820 |
| Deep well waters (average of 157 samples) . | .4378 |

**Hardness of Water.**—Certain of the salts that are very frequently present as impurities in natural waters, give to these waters the property that is known as *hardness*. The chief compounds that produce this effect, are the salts of lime and magnesia. The term *hardness* is applied to such waters, on account of the difficulty of obtaining a lather, with soap, in the ordinary process of washing. Pure soap may be regarded as a mixture of the sodium salts of certain fatty acids (oleic, stearic, palmitic, &c.), which are soluble in pure water. In the presence of salts of lime and magnesium the soap is decomposed; and an insoluble curdy precipitate is formed, by the union of the fatty acid of the soap with the lime and magnesium of the salts. Until the whole of the hardening salts have in this way been thrown out of solution, no lather can be obtained, and the soap is useless as a cleansing agent; but as soon as this point is reached, the addition of any further quantity of soap at once raises a lather on the water, and the soap is capable of acting as a detergent. This process of precipitating the salts of lime and magnesium is known as *softening*, and in this instance the water is softened at the expense of the soap.

Hard waters often become less hard after being boiled for a short time, and this hardness which is so removed is termed the *temporary hardness*. The degree of hardness which the water still possesses after prolonged boiling, is distinguished by the term *permanent hardness*. The diminution of the total hardness of a water by boiling, is due to the fact that the soluble acid carbonates of lime and magnesium are decomposed during this process, into water, carbon dioxide (which escapes as gas), and the practically insoluble normal carbonates of these metals; thus, in the case of the lime salt—

$$CaH_2(CO_3)_2 = H_2O + CO_2 + CaCO_3.$$

When such a water is boiled, the calcium carbonate is thrown down as a white precipitate, which gradually collects upon the bottom of the containing vessel. The "furring" of kettles, and the formation of calcareous deposits in boilers, is largely due to this cause.

In the case of waters that are highly charged with calcium carbonate, held in solution by dissolved carbonic acid, this deposition of calcium carbonate may even take place at the ordinary temperature, owing to the diffusion of the dissolved carbon dioxide into the air. It is in this way that those remarkable, and often beautifully *fantastic, formations, known as stalactites*, have been produced in certain subterranean caves. Water charged with the soluble calcium carbonate, in slowly dropping from the roof of such a cave, loses a portion of its dissolved carbon dioxide, and, in consequence, deposits a certain amount of the calcium carbonate which was in solution. Each drop, as it slowly forms, adds its little share of calcium carbonate to the deposit, which thereby gradually grows, much as an icicle grows, as a dependent mass called a stalactite. Whether the water that drops from the stalactite has deposited the whole of its calcium carbonate, will depend largely upon the time occupied by each drop in gathering and dropping; if, as often happens, the whole has not been precipitated, the remainder is deposited upon the floor of the cave, and a growing column of calcium carbonate, called a *stalagmite*, gradually rises from the ground until it ultimately meets the stalactite.

**Clark's Process for Softening Water.**—Waters whose hardness is due to the presence of the carbonates of lime and magnesium, can be deprived of their hardness by the addition to them of lime. The amount of hardness is first estimated, and such an amount of milk of lime is then added as is demanded by the following equation:—

$$CaH_2(CO_3)_2 + CaO = H_2O + 2CaCO_3.$$

In this way, the soluble lime salt is converted into the insoluble normal carbonate, which settles to the bottom of the tank.

The salts, which are mainly instrumental in causing the permanent hardness, are the sulphates of lime and magnesium. The degree of hardness and its particular order, that is, whether temporary or permanent, will obviously be determined entirely by the particular geological formation from which the water is derived.

**Potable Waters.**—Undoubtedly the most important use to which water is put, is its employment as an article of food to man, and since it has been proved beyond dispute that many virulent diseases, such as cholera, typhoid fever, and others are propagated through the medium of drinking-water, it becomes a matter of the greatest sanitary importance that the waters supplied for this purpose should be as pure as possible. Excepting in very rare instances, where poisonous mineral matters accidentally gain access to drinking-water (as for example, in the case of certain waters which are capable of attacking, and to a slight extent dissolving, the lead of the pipes through which they may be passed), the solid matters that are usually found in waters are not injurious to health. The living germs or bacilli, through whose agency zymotic diseases are caused, cannot be detected in a sample of water by any *direct* chemical or microscopical analysis. A specimen of pure distilled water might be artificially contaminated with such organisms so as to constitute it a most virulent poison, and still chemical analysis would fail to detect the danger, and the water would be pronounced pure. Chemical analysis can, however, reveal the presence of excrementitious matter, and also of the characteristic products resulting from its decomposition: it can with certainty detect in the water the evidence of recent contamination with sewage matters, and it can also, with considerable precision, trace the evidences of its having been so contaminated at an earlier stage of its history. It cannot, however, distinguish between pollution with healthy, and with infected excreta, and therefore it is necessary to regard with the greatest suspicion any water to which sewage has at any time gained access. Waters that are made use of for drinking purposes may be classified in the following order:—

| | |
|---|---|
| Safe . . | 1. Spring water. |
| | 2. Deep well water. |
| | 3. Mountain rivers and lakes. |
| Suspicious | 4. Stored rain water. |
| | 5. Surface water from cultivated land. |
| Dangerous | 6. River water to which sewage gains access. |
| | 7. Shallow well water. |

## HYDROGEN PEROXIDE.

Formula, $H_2O_2$.

**Occurrence.**—This compound is occasionally found in small quantities in the atmosphere, and also in dew and rain.

**Modes of Formation.**—(1.) Hydrogen peroxide is produced in small quantities during the burning of hydrogen in the air. If a jet of burning hydrogen be caused to impinge upon the surface of water, the temperature of which is not allowed to rise above 20°, the water will be found, after a short time, to contain hydrogen peroxide.*

---

* *See* "*Chemical Lecture* Experiments," p. 72.

(2.) This compound is also produced by the decomposition of barium peroxide by carbonic acid. For this purpose a stream of carbon dioxide is passed through ice cold water, into which from time to time small quantities of barium peroxide are stirred. Barium carbonate is precipitated, and a dilute aqueous solution of hydrogen peroxide is obtained—

$$BaO_2 + H_2CO_3 = BaCO_3 + H_2O_2.$$

(3.) Barium peroxide may be decomposed by either hydrochloric, sulphuric, silicofluoric, or phosphoric acid. Whichever acid be employed, the barium peroxide, previously mixed with a small quantity of water, is added gradually to the acid; which, in the case of either hydrochloric or sulphuric acid, should be diluted with from five to ten times its volume of water. The temperature of the mixture is not allowed to rise above 20°. Thus, in the case of hydrochloric acid—

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2,$$

the soluble barium chloride is removed by the addition of sulphuric acid, whereby barium sulphate is precipitated, and hydrochloric acid formed—

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl.$$

The hydrochloric acid may be removed by adding a solution of silver sulphate, which precipitates silver chloride, leaving sulphuric acid in solution—

$$2HCl + Ag_2SO_4 = 2AgCl + H_2SO_4.$$

And, lastly, the free sulphuric acid is withdrawn by the addition of barium carbonate—

$$H_2SO_4 + BaCO_3 = BaSO_4 + H_2O + CO_2.$$

When sulphuric is employed for the decomposition of barium peroxide, the crystallised, or hydrated peroxide ($BaO_2,8H_2O$), is most advantageous for the purpose. This salt, made into a paste with water, is gradually added to the diluted and cooled acid, until the acid is nearly but not quite neutralised. The slight excess of acid is removed by the addition of the exact quantity of barium hydroxide (baryta-water) necessary to neutralise it, and the insoluble barium sulphate is removed by filtration. On a large scale silicofluoric acid, or phosphoric acid, is usually employed, preferably the latter, as it is found that small quantities of free phosphoric acid in hydrogen peroxide greatly retard its decomposition.

(4.) Hydrogen peroxide is also readily obtained by decomposing potassium peroxide by means of tartaric acid. The potassium peroxide is added to a cooled strong aqueous solution of tartaric acid, when potassium tartrate separates out, and an aqueous solution of hydrogen peroxide is obtained.

(5.) When small quantities of hydrogen peroxide are required for the purpose of illustrating its properties, it is most conveniently obtained by adding sodium peroxide to dilute and well-cooled hydrochloric acid, whereby sodium chloride and hydrogen peroxide are formed, both of which remain in solution—

$$Na_2O_2 + 2HCl = 2NaCl + H_2O_2.$$

(6.) Hydrogen peroxide is formed in considerable quantity when ozone is passed through ether floating upon water. Probably a peroxidised compound of ether is first produced, which is then decomposed by the water. This production of hydrogen peroxide may readily be demonstrated by placing a small quantity of water and ether in a beaker, and suspending into the vapour a spiral of platinum wire which has been gently heated. The combustion of the ether vapour upon the wire, whereby the latter is maintained at a red heat, is attended with the formation of ozone, and this acting upon the ether, as already described, results in the production of hydrogen peroxide, which may be detected in solution in the water.

(7.) In small quantities, hydrogen peroxide is produced when moist ether is exposed to the action of oxygen, under the prolonged influence of sunlight.

**Properties.**—The dilute aqueous solution of hydrogen peroxide, obtained by the foregoing methods, is concentrated by evaporation over sulphuric acid in vacuo. In the pure condition it is a colourless and odourless, syrupy liquid, having an extremely bitter and metallic taste. The specific gravity of the liquid is 1.4532. The substance is extremely unstable, giving up some of its oxygen even at temperatures as low as −20°, and decomposing with explosive violence when heated to 100°. Hydrogen peroxide bleaches organic colours, but less rapidly than chlorine. When placed upon the skin it destroys the colour, and gives rise to an irritating blister. When diluted with water, and especially if rendered acid, the compound is far more stable, and in this condition may be preserved at the ordinary temperature for a considerable length of time. When such an aqueous solution is strongly cooled, it deposits ice, and in this way, by the removal of the frozen water, the solution may be concentrated; hydrogen peroxide itself remains liquid at − 30°. When heated the solution is decomposed into water and oxygen—

$$H_2O_2 = H_2O + O.$$

Owing to the readiness with which hydrogen peroxide gives up the half of its oxygen, and is converted into water, its properties are generally those of a powerful oxidising agent. It liberates iodine from potassium iodide; it converts sulphurous acid into sulphuric acid, and oxidises lead sulphide into lead sulphate. Its action upon lead sulphide is made use of, in restoring something of the original brilliancy to oil paintings that have become discoloured. The "white-lead" used in oil paints is gradually converted into lead sulphide when such paintings are exposed to air, especially the air of towns, which is liable to contain small quantities of sulphuretted hydrogen. Lead sulphide being black, the picture slowly assumes a uniformly dark colour, until it is finally quite black. When such a discoloured picture is washed over with dilute hydrogen peroxide, the black sulphide is oxidised into the white lead sulphate—

$$PbS + 4H_2O_2 = 4H_2O + PbSO_4.$$

This compound is employed for bleaching articles that would suffer injury by the use of other bleaching agents, such as ivory, feathers, and even the teeth.

Hydrogen peroxide is also capable of oxidising hydrogen, when that element in the nascent condition is brought in contact with this compound. Thus, if a dilute acidulated solution of hydrogen peroxide be subjected to electrolysis, oxygen will be evolved from the positive electrode, but no gas will be disengaged at the negative pole. The hydrogen, in the presence of the hydrogen peroxide, is oxidised into water—

$$H_2O_2 + H_2 = 2H_2O.$$

Hydrogen peroxide, in many of its reactions, appears to act as a deoxidising agent; thus, manganese dioxide in contact with this substance is reduced to manganous oxide—

$$MnO_2 + H_2O_2 = MnO + O_2 + H_2O.$$

Similarly silver oxide is reduced to metallic silver with the evolution of oxygen—

$$Ag_2O + H_2O_2 = Ag_2 + O_2 + H_2O.$$

In like manner, when ozone is acted upon by hydrogen peroxide, a reaction takes place exactly analogous to that with silver oxide, which will be the more obvious if the formula for ozone be written $O_2O$ instead of $O_3$, thus—

$$O_2O + H_2O_2 = O_2 + O_2 + H_2O.$$

Although, in a sense, these reactions may be regarded as *reducing*, or *deoxidising*, actions, in essence they are not different from those which have been given as illustrative of the oxidising power of hydrogen peroxide. It will be seen that they all depend upon the readiness with which the compound parts with an atom of oxygen, but that in these latter cases the oxygen that is so given up is engaged in oxidising *another atom of oxygen*, contained in the other compound. Thus, in the case of silver oxide, its atom of oxygen is oxidised by the liberated oxygen from the hydrogen peroxide, and converted into the complete molecule of oxygen. By these reactions Brodie first demonstrated the dual, or diatomic, character of the molecule of oxygen.

When hydrogen peroxide is added to a dilute acidulated solution of potassium dichromate, a deep azure-blue solution is obtained (see Chromium), which affords a delicate test for this compound. To apply the test, the dilute hydrogen peroxide is shaken up with ether, and being soluble in this liquid, the ethereal layer which rises to the surface will contain nearly the whole of the peroxide; a few drops of acidulated potassium dichromate are then added, and the mixture again shaken, when the ethereal liquid will separate as a blue layer. In this way, the presence of 0.00025 grammes of hydrogen peroxide in 20 c.c. of water can be detected.

Hydrogen peroxide is decomposed by contact with many substances *which themselves do not* combine with the oxygen; thus charcoal, finely divided palladium, platinum, mercury, and notably silver, when brought into hydrogen peroxide, determine its decomposition into water and oxygen, the rapidity of the action being increased if the liquid be made alkaline. The action is doubtless catalytic, although in all cases the exact *modus operandi* is not clearly understood. In the case of silver it is believed that silver oxide (perhaps peroxide) is first formed, and then decomposed, thus—

$$Ag_2 + H_2O_2 = H_2O + Ag_2O$$
$$Ag_2O + H_2O_2 = H_2O + O_2 + Ag_2.$$

When hydrogen peroxide is added to solutions of the hydroxides of barium, strontium, or calcium, the peroxide of the metal is precipitated—

$$Ba(HO)_2 + H_2O_2 = 2H_2O + BaO_2.$$

The compound is deposited in crystals having the composition $BaO_2,8H_2O$.

With the hydroxides of the alkali metals, the peroxide (which is soluble in water) may be precipitated by the addition of alcohol; when in the case of sodium peroxide, crystals are obtained of $Na_2O_2,8H_2O$.

Hydrogen peroxide is a useful antiseptic: it possesses the advantages of being free from smell, without poisonous or injurious action upon the system, and of leaving as a residue, after having furnished its available oxygen, only water.

# CHAPTER IV

## *NITROGEN*

Symbol, N. Atomic weight = 14.01. Molecular weight = 28.02.

**History.**—Nitrogen was discovered by Rutherford in 1772. He showed that when an animal is placed in a confined volume of air for some time, and the air afterwards treated with caustic potash, to absorb from it the carbon dioxide ("fixed air"), there still remained a gas which was incapable of supporting either respiration or combustion. He called the gas *mephitic air*. Scheele was the first to recognise that this gas was a constituent of the air. Lavoisier applied the name *azote* to the gas, to denote its inability to support life. The name *nitrogen*, signifying the nitre-producer, was suggested by Chaptal, from the fact that the gas was a constituent of nitre.

**Occurrence.**—In the free state nitrogen is present in the atmosphere, of which it forms about four-fifths. Certain nebulæ have been shown, by spectroscopic observation, to contain nitrogen in the uncombined condition. In combination, nitrogen is found in ammonia, in nitre (potassium nitrate), and in a great number of animal and vegetable compounds.

**Modes of Formation.**—(1.) Nitrogen is very readily obtained from the atmosphere, by the abstraction of the oxygen with which it is there mixed.* This is conveniently done by burning a piece of phosphorus in air, confined over water. The phosphorus in burning combines with the oxygen, forming dense white fumes of phosphorous pentoxide, which gradually dissolve in the water, and nitrogen remains in the vessel. The nitrogen obtained in this way is never quite pure, for the phosphorus becomes extinguished before the oxygen is entirely removed; and also the gas will contain atmospheric carbon dioxide.

(2.) Nitrogen in a pure state can be prepared from the atmosphere, by passing a stream of pure air over metallic copper contained in a combustion tube, and heated to redness in a furnace. The air is contained in a gas-holder, and is passed through two U-tubes, the first containing potassium hydroxide (caustic potash), in order to absorb the carbon dioxide; and the second filled with fragments of pumice moistened with sulphuric acid, in order to arrest the aqueous vapour. The purified air, on passing over the heated copper, is deprived of the whole of its oxygen, cupric oxide, CuO, being formed, while pure nitrogen passes on and may be collected.

---

* *Experiments 245, 246,* "Chemical Lecture Experiments."

(3.) Oxygen is rapidly absorbed by a solution of cuprous chloride in hydrochloric acid; a ready method, therefore, of obtaining nitrogen from the air, is to place a quantity of this solution in a stoppered bottle, and shake it up with the contained air. The colourless cuprous chloride solution quickly absorbs the oxygen, becoming dark in colour, and being converted into cupric chloride, the nitrogen of the air remaining in the bottle—

$$Cu_2Cl_2 + 2HCl + O = H_2O + 2CuCl_2.$$

(4.) Nitrogen is obtained by heating a strong solution of ammonium nitrite in a flask, the salt splitting up into water and nitrogen—

$$NH_4NO_2 = 2H_2O + N_2.$$

In practice it is found more convenient to employ a mixture of ammonium chloride and sodium nitrite—

$$NH_4Cl + NaNO_2 = NaCl + 2H_2O + N_2.$$

(5.) By heating a mixture of ammonium nitrate and ammonium chloride, a mixture of nitrogen and chlorine is evolved; the latter gas may be absorbed, by passing the mixture through either milk of lime, or a solution of sodium hydroxide—

$$2NH_4NO_3 + NH_4Cl = 5N + Cl + 6H_2O.$$

(6.) Nitrogen is also evolved when ammonium chromate, or a mixture of potassium dichromate and ammonium chloride, is heated—

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2,$$

or—

$$K_2Cr_2O_7 + 2NH_4Cl = Cr_2O_3 + 2KCl + 4H_2O + N_2.$$

(7.) When ammonia is acted upon by chlorine, it is decomposed, the chlorine combining with the hydrogen to form hydrochloric acid, and the nitrogen being liberated—

$$2NH_3 + 3Cl_2 = 6HCl + N_2.$$

If the chlorine be passed into a strong solution of ammonia, hydrochloric acid which is produced combines with the excess ammonia, forming ammonium chloride; thus—

$$8NH_3 + 3Cl_2 = 6NH_4Cl + N_2.$$

The chlorine, after being washed by passing through water, is bubbled through strong aqueous ammonia contained in a Woulf's bottle. As each bubble of chlorine enters into the ammonia, the combination is attended by a feeble yellowish flash of light and a rapid stream of nitrogen is evolved. The nitrogen, which carries with it dense white fumes of ammonium chloride, should be sc[illegible] by being passed through a second bottle, filled with fragn[illegible] broken glass moistened with water, and it can then be c[illegible] over water in the ordinary way, as shown in Fig. 44.* In preparing nitrogen by this reaction, it is very necessary that the ammonia should be in considerable excess, otherwise there is liable to be formed the dangerously explosive compound of nitrogen and chlorine. See Nitrogen Trichloride.

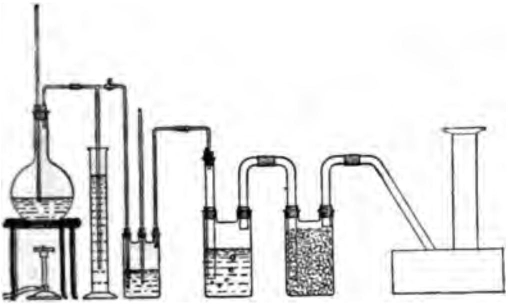

FIG. 44.

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* *Experiment* 252.

**Properties.**—Nitrogen is a colourless gas without taste or smell. It is slightly lighter than air, its specific gravity being 0.972 (air = 1). One litre of the gas at 0° C. and 760 mm. weighs 14 criths, or 1.256 grammes.

Nitrogen is only very slightly soluble in water, its coefficient of absorption at 0° C. being 0.020346.

Nitrogen will not burn, neither will it support the combustion of ordinary combustibles. It is not poisonous, but is incapable of supporting respiration.

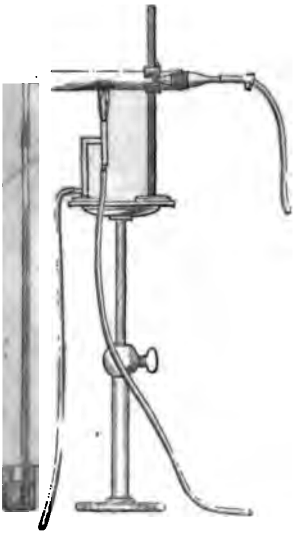

FIG. 45.

Nitrogen is one of the most chemically inert substances known, combining directly, and with difficulty, with only a very few elements. Under the influence of the high temperature of the electric spark it can be made to unite directly with oxygen (see p. 210). Certain metals also combine directly with it, forming nitrides. Thus, when lithium or magnesium are heated in nitrogen, they form respectively $NLi_3$ and $N_2Mg_3$. This reaction may be conveniently shown by means of the apparatus seen in Fig. 45. A small quantity of powdered magnesium is placed in a hard glass tube, which is connected to a long narrow tube dipping into water, and a stream of nitrogen is passed through. When the air is all displaced, the passage of the nitrogen is stopped, and the magnesium strongly heated. At a red heat the nitrogen will be rapidly absorbed, and the water will be seen to rise in the long tube.

The critical temperature of nitrogen is −146°, and when cooled to this point, a pressure of 35 atmospheres causes its liquefaction. Under ordinary atmospheric pressure, the liquid boils at −193°; the gas, therefore, can be liquefied by the cold obtained by the rapid evaporation of liquid oxygen (see p. 176).

# CHAPTER V

## *OXIDES AND OXY-ACIDS OF NITROGEN*

NITROGEN combines with oxygen, forming five oxides :—

| | | |
|---|---|---|
| (1.) | Nitrous oxide (hyponitrous anhydride) . | $N_2O$. |
| (2.) | Nitric oxide . . . . . . . | NO. |
| (3.) | Nitrogen trioxide (nitrous anhydride) . | $N_2O_3$. |
| (4.) | Nitrogen peroxide . . . . . . | $NO_2$ and $N_2O_4$. |
| (5.) | Nitrogen pentoxide (nitric anhydride) . | $N_2O_5$. |

Three oxy-acids of nitrogen are known, corresponding to the three oxides, Nos. 1, 3, 5 :—

| | |
|---|---|
| Hyponitrous acid . . . . . | HNO. |
| Nitrous acid . . . . . . | $HNO_2$. |
| Nitric acid . . . . . . | $HNO_3$. |

The relation in which these three acids stand to their corresponding oxides may be seen by the following formulæ :—

| | | | |
|---|---|---|---|
| Hyponitrous anhydride | $\left.\begin{matrix}N\\N\end{matrix}\right\}O.$ | Hyponitrous acid | $\left.\begin{matrix}N\\H\end{matrix}\right\}O.$ |
| Nitrous anhydride . | $\left.\begin{matrix}NO\\NO\end{matrix}\right\}O.$ | Nitrous acid . | $\left.\begin{matrix}NO\\H\end{matrix}\right\}O.$ |
| Nitric anhydride . | $\left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\}O.$ | Nitric acid . | $\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O.$ |

The most important of all these compounds, and the one from which all the others are directly or indirectly obtained, is nitric acid.

### NITRIC ACID.

Formula, $HNO_3$. Molecular weight = 62.88.

**History.**—Nitric acid, or *aquafortis*, was a well-known and valued *liquid to the alchemists.* Down to the time of Lavoisier

(1776) its true nature was not known; he showed that oxygen was one of its constituents, but as to its other components he was uncertain. Its exact composition was determined by Cavendish.

**Modes of Formation.**—(1.) When an electric spark is passed through a detonating mixture of oxygen and hydrogen with which a certain quantity of air, or nitrogen, is mixed, the water that is produced by the union of the oxygen and hydrogen is found to contain nitric acid. This fact was first observed by Cavendish in the course of his investigations on the composition of water, when, owing to the accidental admixture of air with the mixed gases, oxygen and hydrogen, he found that the water resulting from the union was sometimes acid.

The direct union of nitrogen and oxygen may be brought about by allowing a series of electric sparks to pass between platinum wires, in a confined volume of air, contained in a glass globe, as shown in Fig. 46. In a short time the air in the globe will become distinctly reddish in colour, owing to the formation of nitrogen peroxide. The rapidity of the formation of the red fumes will be greatly increased, by compressing the air within the globe by means of a small compression pump, as indicated in the figure.

If a small quantity of water be introduced, and the contents of the globe shaken up, the red gas will be seen to dissolve in the water, which will then acquire an acid reaction, owing to the formation of nitric acid.

Similarly, when a jet of hydrogen is allowed to burn in air to which additional oxygen has been added, considerable quantities of nitrogen peroxide are formed. The hydrogen may be burnt from a jet, surrounded by a glass tube, as shown in Fig. 47, into which oxygen can be passed by means of the small bent tube at the bottom. On holding a clean dry cylinder over the flame, sufficient of the products of combustion will collect in a few seconds to show the presence of nitrogen peroxide.

(2.) Nitric acid is formed when nitrogenous animal matter undergoes slow oxidation in the air, in the presence of water and an alkali, the nitric acid combining with the alkali to form a nitrate. In this way nitrates are found in the soil, and from the soil often find their way into shallow well waters of towns. In hot and rainless countries these nitrates are sometimes found as crystalline deposits on the surface of the soil, as in Chili and India. (See Potassium Nitrate.)

(3.) Nitric acid is prepared by acting upon potassium nitrate (***nitre-saltpetre***) with sulphuric acid. The nitre is placed in a glass retort, together with an equal weight of sulphuric acid, and the mixture gently heated. The nitric acid readily distils over, and may be collected in a cooled receiver. The residue in the retort consists of hydrogen potassium sulphate—

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3.$$

The acid so obtained is not entirely free from water, and contains nitrogen peroxide in solution, which imparts to it a yellowish-red colour. To purify it, it is again distilled with an equal volume of sulphuric acid; and the redistilled acid is deprived of the last traces of dissolved peroxide of nitrogen, by causing a stream of dry air to bubble through it while slightly warm. Nitric acid so prepared may contain as much as 99.8 per cent. of anhydrous acid, $HNO_3$.

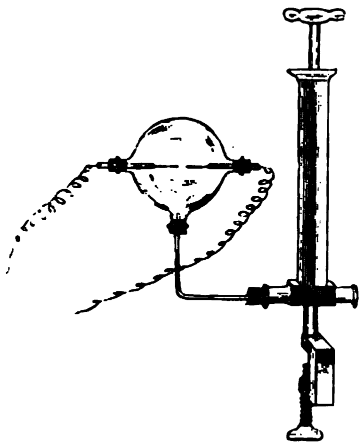

FIG. 46.

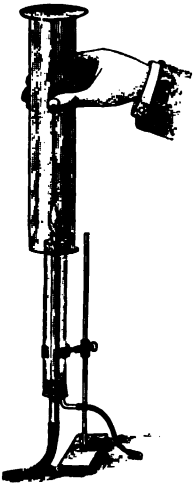

FIG. 47.

(4.) Nitric acid is an article of commercial manufacture. In this process potassium nitrate is replaced by the sodium salt, as being the cheaper material, and the proportion of acid to sodium nitrate employed is arranged in accordance with the equation—

$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3.$$

It will be seen that the whole of the hydrogen of the sulphuric acid has been replaced by the alkali metal, derived from two molecules of the nitrate, and that two molecules of nitric acid result.

The reaction takes place in two stages; in the first we have—

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3.$$

And then, as the temperature is raised, the hydrogen sodium sulphate reacts upon a second molecule of the nitrate, thus—

$$NaNO_3 + NaHSO_4 = Na_2SO_4 + HNO_3.$$

The temperature necessary to effect this second stage, however, causes the decomposition of a certain quantity of the nitric acid itself, thus—

$$2HNO_3 = H_2O + 2NO_2 + O.$$

The retorts usually employed for the manufacture of this acid are large cast-iron cylinders, which are sometimes lined, either entirely or in part, with fireclay, and which are built into a furnace in such a manner as to allow of their being heated as uniformly as possible. The ends of the cylinders are closed by slabs of Yorkshire flag, securely cemented to the iron. The charge of sodium nitrate (Chili saltpetre) and sulphuric acid is introduced through a hole in one end, which is afterwards plugged up, and the vapours are carried off through an earthenware pipe (*c*, Fig. 48), cemented through a hole in the other end, and connected to a series of earthenware pots, *b*, in the manner shown in the figure. The last of these jars is connected with a tower, filled with coke, down which water is caused to percolate, and any peroxide of nitrogen which escapes condensation with the acid in the jars is thereby absorbed.

**Properties.**—Nitric acid is a colourless liquid having a specific gravity of 1.53. It fumes strongly in the air, and has a peculiar and choking smell. It is extremely hygroscopic, absorbing moisture from the air with great readiness. Nitric acid is an intensely corrosive liquid: the strongest acid, when brought in contact with the skin, causes painful wounds, while in more dilute conditions it stains the skin, and other organic materials, a bright yellow colour. A quantity of strong nitric acid thrown upon sawdust causes it to burst into flame. When nitric acid is distilled it first begins to boil at 86°, at the same time it is partially decomposed into water, nitrogen peroxide, and oxygen; the distillate, therefore, ually becomes weaker, and the boiling-point gradually rises. continues until a certain point is reached, when both the erature of the boiling liquid and the strength of the distillate

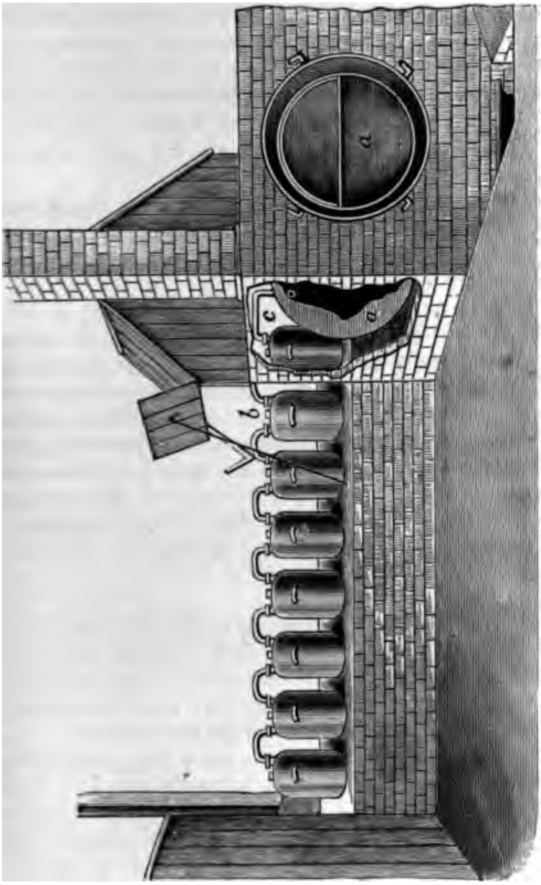

FIG. 48.

ain constant. If, on the other hand, a weak acid be distilled, distillate gradually increases in strength, until when the same nt is *reached, the boiling liquid* has again the same temperature.

This constant boiling-point is 120.5°, and the distillate which comes over at that temperature contains 68 per cent. of $HNO_3$. Whatever the strength of the acid, therefore, on being boiled it loses either nitric acid or water until the strength reaches 68 per cent., and this liquid boils at 120° C. The specific gravity of this acid at 15° is 1.414. It was formerly supposed that the acid of this strength constituted a definite hydrate, but Roscoe has shown that the strength of the acid is purely a function of the pressure, for by varying the pressure under which the distillation is conducted, acids of various compositions can be caused to distil at a constant temperature.

When nitric acid is mixed with water there is a rise in temperature and a contraction in volume, the maximum effect being produced when the mixture is made in the proportion of three molecules of water with one molecule of acid.

Nitric acid is a powerful oxidising agent, on account of the readiness with which it parts with oxygen. Elements such as sulphur and phosphorus are oxidised into sulphuric and phosphoric acids; arsenious oxide into arsenic acid; and many protosalts are converted into persalts. It attacks a large number of metals, forming in many cases the nitrate. Its action upon metals is often of a complicated nature, and depends not only upon the particular metal, but also upon the strength of the acid, the temperature, and the presence of the saline products of the reaction; thus, when nitric acid acts upon copper, the following reaction takes place—

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$$

It is found, however, that as the amount of copper nitrate accumulates, the nitric oxide which is evolved is mixed more and more largely with nitrous oxide, $N_2O$, and even with nitrogen.

Again, when dilute nitric acid acts upon zinc, nitrous oxide is produced, according to the following equation—

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + 5H_2O + N_2O.$$

When, however, strong nitric acid is employed, ammonia is formed, which combines with the excess of acid—

$$4Zn + 9HNO_3 = 4Zn(NO_3)_2 + 3H_2O + NH_3.$$

Owing to the strong oxidising properties of nitric acid, hydrogen is never evolved by the action of metals upon this acid, the hydrogen which is displaced from the acid being converted into water.

The chief reactions of nitric acid may be broadly divided into three classes :—

(1.) With metallic oxides its behaviour is in common with other acids. It exchanges its hydrogen for an equivalent quantity of the metal, forming a nitrate, with the elimination of water, *e.g.*—

$$K_2O + 2HNO_3 = 2KNO_3 + H_2O.$$

(2.) Reactions in which it acts as an oxidising agent; as an example, its action upon iodine, which is converted into iodic acid, may be cited—

$$I + 3HNO_3 = HIO_3 + H_2O + N_2O_3 + NO_2.$$

(3.) Actions in which hydrogen in an organic compound is replaced by the elements $NO_2$, with the elimination of $H_2O$, no gas being evolved. The conversion of cotton-wool, or cellulose, $C_{12}H_{20}O_{10}$, into gun-cotton, or nitro-cellulose, $C_{12}H_{14}O_{10}(NO_2)_6$, is an illustration of this class of reactions—

$$C_{12}H_{20}O_{10} + 6HNO_3 = 6H_2O + C_{12}H_{14}O_{10}(NO_2)_6.$$

Nitric acid is without action upon the so-called *noble* metals, gold and platinum.

Commercial nitric acid, which is of a reddish colour, is liable to contain many impurities: chlorine and iodic acid, derived from the Chili saltpetre; iron, sulphuric acid, and sodium sulphate, carried mechanically over from the retorts; and nitrogen peroxide, from the decomposition of the acid. From these it is purified by redistillation.

Nitric acid is a monobasic acid; the salts of which, known as the nitrates, are for the most part readily soluble in water, and crystallise in well-defined forms. They are all decomposed at a high temperature, evolving oxygen and nitrogen peroxide, or oxygen and nitrogen, leaving an oxide of the metal.

The presence of a nitrate in solution is easily recognised by the following characteristic test. A solution of ferrous sulphate is first added to the solution containing the nitrate, and concentrated sulphuric acid is then cautiously poured down the side of the test-tube, held in a sloping position, so as to fall to the bottom without mixing with the solution. The sulphuric acid acting upon the nitrate, liberates nitric acid; this is reduced by the ferrous sulphate to nitric oxide, which, dissolving in the ferrous sulphate, forms a brown-coloured solution at the point where the two layers of liquid meet. (See Nitric Oxide.)

When nitric acid is added to hydrochloric acid, a mixture is obtained which is known by the name of aqua regia. This name was applied to it by the alchemists on account of its power of dissolving gold. Aqua regia is used in the laboratory for dissolving gold, platinum, and certain ores. Its solvent power depends upon the free chlorine which is evolved from the mixture—

$$HNO_3 + 3HCl = 2H_2O + NOCl + Cl_2.$$

### NITROGEN PENTOXIDE (*Nitric Anhydride*).

Formula, $N_2O_5$. Molecular weight = 107.8.

**Modes of Formation.**—(1.) By withdrawing from nitric acid the elements of water, by means of phosphorus pentoxide—

$$2HNO_3 + P_2O_5 = 2HPO_3 + N_2O_5.$$

For this purpose the strongest nitric acid is cautiously added to phosphorus pentoxide in a cooled retort, in the proportion demanded by the equation; the mixture being made as far as possible without rise of temperature. The pasty mass is then gently heated, when the nitrogen pentoxide distils over, and, if collected in a well-cooled receiver, at once crystallises.

(2.) The method adopted by Deville, who discovered this compound (1849), was by passing dry chlorine over dry silver nitrate contained in a U-tube, which was kept at the desired temperature by being immersed in a water-bath. The following equation expresses the final result of the action—

$$2AgNO_3 + Cl_2 = 2AgCl + N_2O_5 + O.$$

**Properties.**—Nitrogen pentoxide is a white solid substance, crystallising in brilliant prismatic crystals, which melt at 30° with partial decomposition. Between 45° and 50° it undergoes rapid decomposition, evolving brown fumes. It is a very unstable compound; when suddenly heated it decomposes with explosive violence, and even at ordinary temperatures decomposition slowly takes place. It absorbs moisture rapidly, and when thrown into water it dissolves with the evolution of great heat—

$$N_2O_5 + H_2O = 2HNO_3.$$

When nitrogen pentoxide is gradually mixed with nitric acid, a compound is formed having the composition $2N_2O_5,H_2O$; which separates, on cooling, as a definite crystalline hydrate.

## NITROGEN PEROXIDE.

Formula, $NO_2$ and $N_2O_4$. Molecular weight = 45.92 and 91.84.
Density = 22.96 and 45.92.

**Modes of Formation.**—(1.) This compound may be prepared by mixing one volume of oxygen with two volumes of nitric oxide, and passing the red gas so obtained through a tube surrounded by a freezing mixture—

$$2NO + O_2 = 2NO_2.$$

(2.) The nitrates of certain metals, when heated, are decomposed into nitrogen peroxide, oxygen, and an oxide of the metal; thus, if dry lead nitrate be heated in a retort, and the gaseous products of decomposition are conducted into a U-tube placed in a freezing mixture, the nitrogen peroxide collects in the tube—

$$Pb(NO_3)_2 = PbO + N_2O_4 + O.$$

(3.) When arsenious oxide is gently warmed with nitric acid, a mixture of nitric oxide, NO, and peroxide, $NO_2$, is evolved, and if this gaseous mixture be passed through a cooled tube, it condenses to a blue liquid. On passing a stream of oxygen through this liquid it loses its blue colour, and is converted into a yellowish liquid, which consists of nitrogen peroxide.

**Properties.**—At low temperatures nitrogen peroxide is a colourless crystalline compound. It melts at $-9°$, but requires a temperature as low as $-30°$ to solidify it. At a temperature slightly above its melting-point the liquid begins to acquire a pale yellowish tint, which rapidly deepens, until at the ordinary temperature it is a full orange colour. The liquid boils at 22°, and gives a vapour having a reddish brown colour. The colour of the vapour becomes deeper as its temperature is raised, until at 40° it dark chocolate brown, and almost opaque. On allowin vapour to cool the reverse changes take place. This chan colour, as the temperature rises, is accompanied by a s change in the density of the gas, as will be seen from the tabl

| Temperature. | Density, H = 1. | Percentage of $NO_2$ Molecules. |
|---|---|---|
| 26.7° | 38.3 | 20.00 |
| 60.2° | 30.1 | 52.04 |
| 100.1° | 24.3 | 89.23 |
| 135.0° | 23.1 | 98.69 |
| 140.0° | 22.96 | 100.00 |

The density required by the formula $N_2O_4$ is 45.92, while demanded by the formula $NO_2$ is 22.96; hence as the tempe rises a process of dissociation goes on, in which $N_2O_4$ mol are broken down into molecules of the simpler compos At 140° this process is complete, and the gas is entirel solved into $NO_2$. It is believed that at low temperatures, nit peroxide has the composition represented by the formula but that dissociation begins to take place even during the st liquidity, as indicated by the gradual change of colour; and t fore at temperatures between the boiling-point of the liquid 22°, and 140°, the gas consists of mixtures of molecules of NO $N_2O_4$. The calculated percentage of $NO_2$ molecules, whic gas contains at the temperatures at which the above densiti taken, are given in the third column.

Nitrogen peroxide is decomposed by water. At low tem tures, and with small quantities of water, nitric and nitrous are the products of the action, thus—

$$N_2O_4 + H_2O = HNO_3 + HNO_2.$$

At the ordinary temperature, and with an excess of wate following reaction takes place—

$$3NO_2 + H_2O = 2HNO_3 + NO.$$

Gaseous nitrogen peroxide is incapable of supporting the bustion of a taper. Phosphorus, when strongly burning *plunged into* the gas, continues its combustion with brill the temperature of the burning phosphorus being sufficiently high to effect the decomposition of the gas. Nitrogen peroxide is a suffocating and highly poisonous gas, and even when largely diluted with air rapidly produces headache and sickness.

Nitrogen peroxide unites directly with certain metals, giving rise to a remarkable series of compounds, to which the name nitro-metals, or metallic nitroxyls, may be given (Sabatier and Senderens).[*] Thus, when the vapour of nitrogen peroxide is passed over metallic copper (obtained by the reduction of copper oxide in a stream of hydrogen), the gas is rapidly absorbed by the metal with considerable rise of temperature, and a solid brown compound is formed. This substance is the copper-nitroxyl, and its composition is expressed by the formula $Cu_2NO_2$.

Copper-nitroxyl is a fairly stable compound, and is unacted upon by dry air. It is decomposed by water and by nitric acid, hence in its preparation care must be taken to free the nitrogen peroxide from these substances.

At a temperature of about 90° copper-nitroxyl is decomposed into copper and nitrogen peroxide. If, therefore, a quantity of the compound be sealed up in a bent glass tube, and the empty limb of the tube be immersed in a freezing mixture while the compound is gently warmed, the nitrogen peroxide which is evolved will be condensed in the cold portion of the tube.

Similar compounds are formed with the metals cobalt, nickel, and iron.

**Nitrous Acid,** $HNO_2$.—This substance is not known in the pure state. Even in dilute aqueous solution it rapidly decomposes into nitric acid, nitric oxide, and water—

$$3HNO_2 = HNO_3 + 2NO + H_2O.$$

The solution of this acid sometimes acts as a reducing agent, taking up oxygen from such highly oxidised compounds as permanganates, or chromates, and passing into nitric acid—

$$HNO_2 + O = HNO_3.$$

Under other conditions it exerts an oxidising action, as when it bleaches indigo, or liberates iodine from potassium iodide, being itself reduced to nitric oxide and water, with the elimination of oxygen—

$$2HNO_2 = 2NO + H_2O + O.$$

The salts of nitrous acid, viz., the *nitrites*, are stable compounds. The nitrites of the alkalies are best prepared by carefully heating the nitrates; thus, when potassium nitrate is fused, it parts with oxygen, and is transformed into potassium nitrite—

---

[*] *Bulletin de la Société Chimique*, September 1893.

$$KNO_3 = KNO_2 + O.$$

At a higher temperature the nitrite is also decomposed.

Nitrites are decomposed by dilute acids, evolving brown vapours, and in this way are at once distinguished from nitrates.

**Nitrogen Trioxide.**—There is considerable doubt as to the existence of this compound. It has been usually stated that it is formed by the action of nitric acid upon arsenious oxide, according to the equation—

$$As_4O_6 + 4HNO_3 = 2As_2O_5 + 2H_2O + 2N_2O_3.$$

It has, however, been shown by the determination of the vapour density, that in the gaseous state the compound $N_2O_3$ does not exist, but that the gas is a mixture of molecules of NO and $NO_2$. It will be seen that a mixture containing equal volumes of these two gases will have a composition represented by the formula $N_2O_3$, therefore the above reaction may be regarded as taking place thus—

$$As_4O_6 + 4HNO_3 = 2As_2O_5 + 2H_2O + 2NO + 2NO_2.$$

Simultaneously with this reaction the following decomposition also goes forward—

$$As_4O_6 + 8HNO_3 = 2As_2O_5 + 4H_2O + 8NO_2.$$

The result, therefore, of the action of nitric acid upon arsenious oxide is a mixture of nitric oxide and peroxide in varying proportions.

When this mixture is strongly cooled, it condenses to a blue liquid, believed by some to be the true compound $N_2O_3$. Others regard it as merely a solution of the difficultly liquefiable gas, NO, in liquid nitrogen peroxide, $NO_2$. If the two oxides are in a state of combination, it would appear to be at best a feeble union, for it has been shown that at temperatures as low as −90° the liquid slowly evolves NO, while at this temperature no nitrogen peroxide is given off.

## NITRIC OXIDE.

Formula, NO. Molecular weight = 29.96. Density = 14.96.

**History.**—Nitric oxide was first obtained by Van Helmont. Priestley, however, was the first to investigate this gas, which he termed *nitrous air*, and which was employed by him in his analysis of air.

**Modes of Formation.**—(1.) This gas is obtained by the action of nitric acid of specific gravity 1.2 upon copper or mercury. In practice, copper is always employed.* The action may be represented thus—

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$$

The gas obtained by this method is always liable to contain nitrous oxide, and even free nitrogen; the amount of these impurities rapidly increasing if the temperature be allowed to rise, and still more so as the amount of copper nitrate in solution increases.

(2.) Pure nitric oxide is readily obtained by the action of nitric acid upon ferrous sulphate. The reaction is best applied by generating the nitric acid from potassium nitrate and sulphuric acid in the presence of ferrous sulphate. A mixture of the two salts, in the proportion of about one part of nitre to four of ferrous sulphate, is introduced into a flask, with a small quantity of water. Strong sulphuric acid is dropped upon the mixture by means of a dropping funnel, and the mixture gently warmed, when a steady stream of pure nitric oxide is evolved—

$$2KNO_3 + 5H_2SO_4 + 6FeSO_4 = 2HKSO_4 + 3Fe_2(SO_4)_3 + 4H_2O + 2NO.$$

A precisely similar result may be obtained by the reduction of potassium nitrate by means of ferrous chloride in the presence of hydrochloric acid, thus—

$$KNO_3 + 3FeCl_2 + 4HCl = 3FeCl_3 + KCl + 2H_2O + NO.$$

**Properties.**—Nitric oxide is a colourless gas, having a specific gravity of 1.039. When brought into the air, it combines with the atmospheric oxygen, forming red brown vapours, consisting of a mixture of nitrogen tri- and per-oxides, the combination being attended with a rise of temperature. The formation of these red fumes in contact with oxygen, is characteristic of this gas, thereby distinguishing it from all other gases. This property of nitric oxide renders it impossible to ascertain whether this gas has any smell, or is possessed of any toxicological action. Nitric oxide is only very sparingly soluble in water. It is the most stable of all the oxides of nitrogen, being able to stand a dull red heat without decomposition. It is not a supporter of combustion. A lighted taper, or a burning piece of sulphur, when introduced into the gas, are extinguished. If the temperature of the burning substance is sufficiently high to decompose the gas, combustion then continues at the expense of the liberated oxygen: thus, if a piece of phosphorus, which is freely burning in the air, be plunged into this gas, it continues its combustion with great brilliancy; if, however, the phosphorus be only feebly burning when thrust into the gas, it is at once extinguished. A mixture of carbon disulphide vapour and nitric oxide, obtained by allowing a few drops of the liquid to fall into a cylinder of the gas, burns, when inflamed, with an intensely vivid bluish flame, which is especially rich in the violet or *actinic* rays, and has on this account been sometimes employed by photographers to illuminate dark interiors. Nitric oxide is soluble in a solution of ferrous sulphate, forming a dark brown solution, containing an unstable compound of ferrous sulphate and nitric oxide, $2FeSO_4,NO$. This compound is readily decomposed by heat, nitric oxide being evolved. By means of this reaction, nitric oxide may be separated from other gases. Nitric oxide is a difficultly liquefiable gas, its critical temperature being $-93.5$: at this temperature a pressure of 71.2 atmospheres is required to liquefy it.

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* *Experiment 297,* "*Chemical* Lecture Experiments."

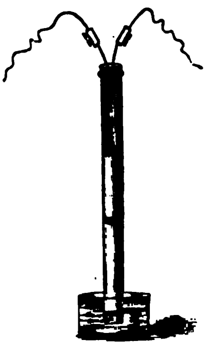


FIG. 49.

The composition of nitric oxide may be proved, by heating a spiral of iron wire by means of an electric current, in a measured volume of the gas (as shown in Fig. 49).* As the metal becomes red hot the gas is gradually decomposed, and the oxygen combines with the iron to form ferric oxide. The residual nitrogen will be found to occupy one-half the original volume.

| | |
|---|---|
| Two vols. of nitric oxide, weighing | 29.96 |
| Contain 1 vol. of nitrogen, weighing | 14.00 |
| | 15.96 = weight of 1 vol. of oxygen. |

Therefore we learn that two volumes of nitric oxide consist of one volume of nitrogen and one volume of oxygen united without condensation.

---

* Experiment 304.

## NITROUS OXIDE (*Hyponitrous anhydride, Laughing gas*).

Formula, $N_2O$. Molecular weight = 43.96. Density = 21.98.

**History.**—This gas was discovered by Priestley, and called by him *dephlogisticated nitrous air*.

**Modes of Formation.**—(1.) Nitrous oxide is formed by the reduction of nitric acid by certain metals, as zinc or copper, under special conditions (see Nitric Acid). These reactions, however, are never made use of for the preparation of the gas for experimental purposes.

(2.) The most convenient method for obtaining this compound is by the decomposition of ammonium nitrate. A quantity of the dry salt is gently heated in a flask fitted with a cork and delivery-tube. The salt rapidly melts and splits up into nitrous oxide and water—

$$NH_4NO_3 = 2H_2O + N_2O.$$

The heat should be carefully regulated, or the decomposition is liable to become violent, in which case nitric oxide is also evolved. Nitrous oxide being rather soluble in cold water, the gas should be collected either over mercury, or over hot water.

When the gas is to be used for anæsthetic purposes, it should be purified by being passed first through a solution of ferrous sulphate to absorb any nitric oxide, and afterwards through caustic soda, to remove any chlorine which may have been derived from the presence of ammonium chloride in the nitrate.

**Properties.**—Nitrous oxide is a colourless gas, having a faint and not unpleasant smell, and a peculiar sweetish taste. Its specific gravity is 1.52. The gas is somewhat soluble in water, its coefficient of absorption at 0° being 1.3052. The solubility rapidly decreases as the temperature rises, as will be seen by the following table (Carius):—

| 1 c.c. Water at 760 mm. Dissolves | c.c. $N_2O$ at 0° C. and 760 mm. |
|---|---|
| At 0° | 1.3052 |
| „ 10° | 0.9196 |
| „ 20° | 0.6700 |
| „ 25° | 0.5962 |

The loss of gas during its collection over water in the pneumatic trough, arising from its *solubility in that liquid*, is therefore greatly lessened by using warm water. Nitrous oxide is much more readily decomposed than nitric oxide, a red hot splint of wood is instantly rekindled, and bursts into flame when plunged into the gas. Phosphorus burns in it with a brilliancy, scarcely perceptibly less dazzling than in pure oxygen. If a piece of sulphur, which is only feebly burning, be thrust into a jar of this gas, the sulphur is extinguished, the temperature of the flame not being sufficiently high to decompose the gas. When, however, the sulphur is allowed to get into active combustion before being placed in the gas, the combustion continues with greatly increased brilliancy. In all cases of combustion in nitrous oxide, the combustion is simply the union of the burning body with oxygen, the nitrogen being eliminated. From its behaviour towards combustibles, nitrous oxide might readily be mistaken for oxygen; it can, however, be easily distinguished from that gas by the fact that when added to nitric oxide it does not produce red vapours, whereas when oxygen is mixed with nitric oxide these coloured gases are instantly formed.

When equal volumes of nitrous oxide and hydrogen are mixed in a eudiometer, and an electric spark passed through the mixture, the gases combine with explosion, water being produced and nitrogen set free; the volume of nitrogen so resulting being equal to that of the nitrous oxide employed. This compound, therefore, contains its own volume of nitrogen, and half its own volume of oxygen. Nitrous oxide, when inhaled, exerts a remarkable action upon the animal organism. This fact was first observed by Davy. If breathed for a short time, the gas induces a condition of hysterical excitement, often accompanied by boisterous laughter, hence the name laughing gas. If the inhalation be continued, this is followed by a condition of complete insensibility, and ultimately by death. On account of the ease with which the state of insensibility can be brought about, this gas is extensively employed as an anæsthetic, especially in dentistry.

Nitrous oxide is a gas which is moderately easily liquefied; at 0° C. a pressure of thirty atmospheres is required to effect its liquefaction.

Liquid nitrous oxide is colourless and mobile; it boils at $-92°$, and when dropped upon the skin produces painful blisters. When thrown upon water, a quantity of the water is at once converted into ice: mercury poured into a tube containing a small quantity of the liquid is instantly frozen. An ignited fragment of charcoal thrown upon the liquid floats upon the surface, at the same time burning with brilliancy. If the liquid be mixed with carbon disulphide, and placed in vacuo, the temperature falls to −140. By strongly cooling the liquid, contained in a sealed tube, Faraday succeeded in solidifying it; this may also be effected by the rapid evaporation of the liquid. The solid melts at −99°, and if placed upon the hand causes a painful blister; in this respect it differs from solid carbon dioxide, which gasifies without previous liquefaction.

**Hyponitrous Acid,** NHO.—This substance has not yet been isolated, being only known in its salts and in aqueous solution.

When a solution of potassium nitrate, or nitrite, is acted upon by sodium amalgam (an alloy of sodium and mercury), the salt is reduced by the nascent hydrogen, evolved by the action of the amalgam upon water, and the potassium salt of hyponitrous acid is left in solution—

$$KNO_3 + 2H_2 = 2H_2O + KNO.$$

The solution, which is alkaline, owing to the presence of sodium hydroxide, is then made neutral by the addition of acetic acid, and silver nitrate added. A yellow precipitate is thrown down, consisting of silver hyponitrite, AgNO.

When a solution of potassium hyponitrite is acidified and then heated, the hyponitrous acid, which may be regarded as liberated by the acid, is broken up into nitrous oxide and water—

$$2HNO = N_2O + H_2O.$$

**Nitrosyl Chloride,**[*] NOCl.—This compound may be obtained by the direct combination of nitric oxide with chlorine—

$$2NO + Cl_2 = 2NOCl.$$

It is also formed by the action of phosphorus pentachloride upon potassium nitrite, thus—

$$PCl_5 + KNO_2 = NOCl + POCl_3 + KCl.$$

Nitrosyl chloride is formed together with chlorine when a mixture of nitric and hydrochloric acids is gently heated—

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O.$$

Nitrosyl chloride is also readily prepared by the action of nitrosyl hydrogen sulphate upon dry sodium chloride, thus—

$$(NO)HSO_4 + NaCl = NOCl + NaHSO_4.$$

**Properties.**—Nitrosyl chloride is an orange-yellow gas, which easily condenses when passed through a tube immersed in a freezing mixture, to an

---

[*] Tilden has shown that this is the *only oxy-chloride* of nitrogen that exists.

orange-yellow liquid, which boils at about − 8°. It is decomposed by
into nitrous acid and hydrochloric acid—

$$NOCl + H_2O = HNO_2 + HCl.$$

In a similar manner it is decomposed by metallic oxides and hydro
thus—

$$NOCl + 2KHO = KNO_2 + KCl + H_2O.$$

Nitrosyl chloride has no action upon gold and platinum, but it a
mercury with the formation of mercurous chloride and the liberation of
oxide—

$$2NOCl + Hg_2 = Hg_2Cl_2 + 2NO.$$

# CHAPTER VI

## *THE ATMOSPHERE*

ıosphere is the name applied to the gaseous mixture velops the earth, and which is commonly called the air. r chemists used the word *air* much as in modern times . *gas* is employed; thus they spoke of inflammable air, ;ticated air, alkaline air, and so on.

r consists of a mixture of gases, the two chief ingredients trogen and oxygen. Lavoisier was the first to clearly at oxygen was a constituent of the air, although Robert d others before him had shown, that air was absorbed by ı the process of forming a *calx*, and that the metal gained s the calx formed. When the fact that the air was com- oxygen and nitrogen became established, various devices opted to determine the proportion of oxygen in it. 's method was by means of nitric oxide. It depended : fact that when nitric oxide is mixed with air, it combines oxygen, forming brown fumes which dissolve in the water. ıction in volume therefore takes place, from which the ıf oxygen may be calculated. This method yielded results emed to show that there was considerable variation in the ›n of oxygen present in different samples of air, and the se that the wholesomeness, or goodness, of the air was ıt upon the quantity of oxygen which it contained. Hence e term *eudiometry*, signifying *to measure the goodness*. ıh, on the other hand, as the result of a large number of :nts made by him, came to the conclusion that there was :nce in the samples of air that he experimented upon.

the time of Cavendish, eudiometric analysis has been to a state of great perfection and accuracy by Bunsen, t, Frankland, and others. The conclusion to be drawn : extended researches of these chemists is, that although ›sphere certainly shows a remarkable uniformity of com- there do *exist perceptible*, though very slight, variations

in the amount of oxygen present at different places and at differ
times. Samples of air collected from all parts of the globe, fr

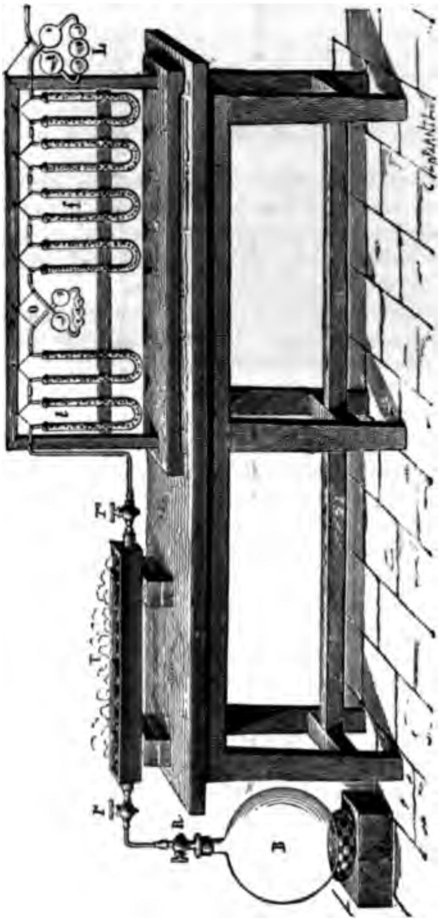


FIG. 59.

mid ocean, from high mountain peak, American prairie, a
crowded cities, show a variation in the proportion of oxygen ra
ing from 20.99 to 20.86. Angus Smith has shown, that in fog

weather the oxygen in the air in towns, sometimes falls as low as 20.82. Samples of air taken from crowded theatres, have been found to contain as little as 20.28, while in many mines the amount averages as low as 20.26.

The mean proportions of oxygen and nitrogen in the atmosphere may be given as—

| | |
|---|---|
| Oxygen . . . . . | 20.96 parts by volume. |
| Nitrogen . . . . . | 79.04 „ „ |
| | 100.00 |

The composition of the atmosphere by weight was determined by Dumas and Boussingault (1841). In their method, air which was freed from carbon dioxide and moisture, was slowly drawn through a glass tube containing a known weight of metallic copper, heated to redness. The oxygen combined with the copper, forming copper oxide, which was afterwards weighed, and the nitrogen passed into a vacuous flask, and was also weighed. The apparatus as employed by Dumas is seen in Fig. 50. B is a glass flask having a capacity of 10 to 15 litres, which was exhausted and then weighed. It was then attached, as shown, to the tube T, containing a known weight of metallic copper, and which was also exhausted. The bulbs L contained a solution of potassium hydroxide, and the tubes *f*, solid potash, for the removal of atmospheric carbon dioxide. The bulbs O contained strong sulphuric acid, and the tubes *t* were filled with pumice moistened with the same acid, by means of which the moisture was withdrawn from the air. When the copper was heated and the cocks partially opened, air, free from carbon dioxide and moisture, was slowly drawn over the heated metal, which was thereby converted into the oxide. At the conclusion of the experiment the globe and the tube T were reweighed. The nitrogen remaining in tube T was then pumped out and the tube once more weighed. The difference between the two last weighings of the tube, added to the gain in weight suffered by the globe, gave the nitrogen; while the difference between the original and final weights of the tube gave the increase of weight suffered by the copper, that is, the amount of oxygen. The result of numerous experiments gave the mean composition—

| | |
|---|---|
| Oxygen . . . . . . | 23 parts by weight. |
| Nitrogen . . . . . . | 77 „ „ |
| | 100 |

A more modern method for estimating the amounts of oxygen and nitrogen in the air, based upon the same principle, namely, the absorption of the oxygen by heated metallic copper, is illustrated in Fig. 51 (known as Jolly's apparatus). The sample of air to be examined is allowed to enter the glass globe A (whose capacity is about 100 c.c., and which has been previously exhausted) by means of the three-way cock *b*. (The air is first dried, by being drawn through tubes filled with pumice moistened with sulphuric acid, on its way into the apparatus.) The bulb is then surrounded by the metal jacket B, which is filled with broken ice, and when the temperature has fallen to 0° the bulb is put into communication with the tube *d* by means of the three-way cock. The tube *g* is then raised or lowered, so as to bring the mercury in *d* to a fixed point in the tube at *m*, and the tension of the enclosed air is ascertained by the graduated scale behind tube *g*. The ice-jacket is then removed, and the spiral of copper wire within the bulb is heated

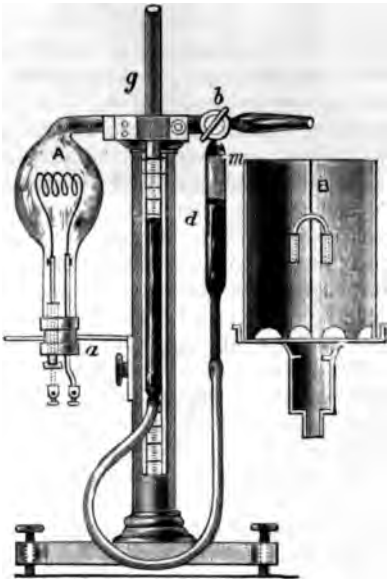


FIG. 51.

to redness by the passage through it of an electric current. The copper combines under these conditions with the oxygen, forming copper oxide, thereby reducing the volume of the contained gas. The globe is again cooled, and the tube *g* lowered to such a position, that when communication is once more made between the globe and tube *d*, the mercury shall stand at the same point *m*.

From the observed tension of the gas before and after the experiment, the volume relations of the two constituents can be calculated. Thus, suppose the tension of the enclosed air to be 720.25 mm., and that of the residual nitrogen 569.28 mm., then for 1 volume of air the reduction would be—

$$\frac{569.28}{720.25} = .7904 \text{ vols.}$$

Therefore in 100 volumes the composition would be—

$$\begin{aligned} \text{Nitrogen} &= 79.04 \\ \text{Oxygen} &= \underline{20.96} \\ & \quad 100.00 \end{aligned}$$

Besides oxygen and nitrogen, the air contains variable quantities of the following gases: carbon dioxide, aqueous vapour, ammonia, ozone, nitric acid. With the exception of aqueous vapour, these substances are present only in relatively small proportions, and with *all* of them the amount is liable to considerable variation. Especially is this the case with the aqueous vapour, as the amount of this constituent present at any time is largely influenced by the temperature. The average composition of normal air may be taken as follows:—

| | Vols. per 1000. |
|---|---|
| Nitrogen . . . . . | 779.0600 |
| Oxygen . . . . . | 206.5940 |
| Aqueous vapour . . . | 14.0000 |
| Carbon dioxide . . . | 0.3360 |
| Ammonia . . . . . | 0.0080 |
| Ozone . . . . . . | 0.0015 |
| Nitric acid . . . . | 0.0005 |
| | 1000.0000 |

**Aqueous Vapour.**—For any given temperature there is a maximum amount *of aqueous vapour*, which a given volume of air is capable of taking up: under these conditions the air is said to be *saturated with moisture* at the particular temperature. The cubic metre of air is saturated with moisture at the various temperatures stated, when it has taken up the following weights of water:—

| | | | |
|---|---|---|---|
| At 0° | 4.871 grammes. | At 20° | 17.157 grammes. |
| " 10° | 9.362 " | " 30° | 30.095 " |

When air, saturated with moisture at say 20°, is cooled to 10°, the excess of water beyond 9.362 (the maximum for 10°) is deposited either as mist or rain. The temperature at which air thus begins to deposit moisture is called the *dew-point*. The deposition of moisture from the air caused by the lowering of the temperature is a matter of everyday observation. A glass vessel containing iced water, becomes bedewed with moisture upon the outside, as the air in its immediate vicinity is cooled. When a season of severe frost is suddenly followed by a warm wind, highly charged with aqueous vapour, it is not unusual to see condensed moisture collecting upon, and streaming down, the cold surface of walls. For the same reason, after the sun has set, and the heat from the ground has radiated, leaving the ground colder than the atmosphere, the temperature of the air is lowered, and it begins to deposit its aqueous vapour in the form of dew.

The amount of aqueous vapour in the air, or the humidity of the air, is estimated by meteorologists by means of an instrument called the wet and dry bulb thermometer.

**Carbon Dioxide.**—The proportion of this gas present in the air is also liable to considerable variation, although not through such a wide range as the aqueous vapour. The processes of respiration, combustion, and putrefaction are attended by the evolution of carbon dioxide, hence the amount of this gas present in closed inhabited places, is greater than that in the open air; in badly ventilated and crowded rooms, the proportion sometimes rises to three parts in 1000 vols. Frankland has found that at high elevations the amount of carbon dioxide in the air is often, although not invariably, considerably above the normal.

| | | | | | |
|---|---|---|---|---|---|
| At Chamounix (3000 feet) | the amount of | carbon dioxide | was 0.63 | per | 1000 vols. |
| " Grands Mulets (11,000 feet) | " | " | " 1.11 | " | " |
| " Mont Blanc (15,732 feet) | " | " | " 0.61 | " | " |

This fact is probably due to the absence, in these high regions, f the vegetation which is one of the chief natural causes operating o remove atmospheric carbonic dioxide (see Oxygen, page 166).

The amount of carbon dioxide is slightly higher during the night, and often rises considerably during foggy weather. Thorpe has shown that near the surface of the sea, the amount of carbon dioxide in the air is slightly less, being on an average 0.300 vols. per 1000.

**Ammonia** in the atmosphere is derived from the decomposition of nitrogenous organic matter. Although present in relatively very small quantities, it varies in amount very considerably. From the experiments of Angus Smith, 1000 grains of air from various sources were found to contain the following amounts of ammonia :—

| | |
|---|---|
| London . . . | 0.05 grammes. |
| Glasgow . . . | 0.06 „ |
| Manchester . . . | 0.10 „ |

The proportion of ammonia appears to be higher during the night than in the daytime, and immediately after heavy rain the amount is perceptibly diminished.

Rain water always contains ammonia, although the amount varies greatly with changing atmospheric and climatic conditions. Lawes and Gilbert, Angus Smith, and others, have made a large number of estimations of the amount of ammonia in rain water at various places and seasons, and under many different conditions.

**Nitric Acid**, present in the form of nitrates and nitrites, is produced in the atmosphere by the direct union of oxygen and nitrogen whenever a lightning flash passes through the air (see Nitric Acid). Rain which falls during or immediately after a thunderstorm is found to contain nitrates and nitrites.

These two nitrogenous compounds, ammonia and nitric acid, although present only in such small proportion in the atmosphere, fulfil a most important function in the economy of nature. From the experiments of Lawes and Gilbert and others, it has been shown, that most plants are unable to draw upon the free nitrogen of the atmosphere, for the supply of that element which they require for the development of their structure and fruit.* Although they are surrounded by, and bathed in, nitrogen, they cannot assimilate it. Plants that are growing in unmanured soil, therefore, derive their nitrogen from the ammonia and nitric acid which are present in the air, and which are washed into the ground by the rain. It has been found that a plant grown under such experimental conditions as to exclude the possibility of its obtaining supplies of these nitrogenous compounds, will yield upon analysis exactly the same amount of nitrogen as was originally contained in the seed from which it grew.

---

* Leguminous plants, such as clovers, vetches, beans, peas, which develop root-nodules *or tubercles, are exceptions.*

**Ozone.**—The causes which operate in the formation of this substance in the air are at present imperfectly known : it is supposed that its occurrence is related to the development of electricity in the atmosphere. On account of the powerful oxidising character of ozone, its presence can never be detected in the air, where much organic matter of an oxidisable nature is present, as is the case in the air of such places as malarial swamps, dwelling-houses, and large towns.

The amount of ozone in pure country air has been found to vary with the time of year, reaching a maximum in the spring-time, and gradually falling towards winter. Thorpe has found that in sea air the amount of ozone is practically constant during all seasons.

The usual method which is available for the detection and estimation of ozone in the air is extremely crude. It consists in exposing ozone test-papers (see Ozone) to the air for a certain time, and comparing the colour that is produced with a standard scale of tints : moreover, other substances than ozone, which may be present in the atmosphere, will also liberate iodine from potassium iodide, and these are therefore measured as ozone. Besides the higher oxides of nitrogen, which, as we have seen, are formed in the atmosphere, and which liberate iodine from potassium iodide, it has been shown that peroxide of hydrogen is also present. The state of our knowledge at present, therefore, respecting the exact amount of atmospheric ozone, and its variation, is far from satisfactory ; it is, indeed, quite possible that many of the effects which have been attributed to ozone, are in reality due to peroxide of hydrogen. Thus it has been shown by Schönbein that this compound is formed during the evaporation of water, and this statement probably derives confirmation from the fact that its presence may be detected in rain water. The salubrity of the air of the sea-shore, where large areas of wet sand and stones offer the most perfect conditions for the rapid evaporation of water, and, consequently, for the formation of peroxide of hydrogen, may therefore be attributable as much to the presence of this substance as to the proverbial ozone.

The various gases of which the air is composed, are not combined, but are merely mingled together. The remarkable constancy of its composition, as regards the oxygen and nitrogen, led chemists at one time to suppose, that these gases were in chemical union with each other in the atmosphere; but a number of facts which have since been learnt respecting these gases, prove without doubt that this is not the case, and that the air is simply a mechanical mixture. This evidence may be briefly summed up as follows:—

(1.) When oxygen and nitrogen are mixed together in the proportion in which they occur in air, the resulting mixture behaves in all respects like ordinary air, and the mixing of the gases is not attended by any volumetric or thermal disturbance, such as would be expected to accompany the chemical union of two elements.

(2.) The degree to which air is capable of refracting light, is found to be the mean of the refractive power of oxygen and nitrogen. Were these gases chemically combined, the compound should behave in this respect as other compound gases, where it is found that the refractive index is always either greater or less than the mean of that of the constituents.

(3.) According to a fundamental law of chemical science, the composition of a chemical compound is constant. Such a thing as variability in the composition of a compound is unknown. The proportion of oxygen and nitrogen, as we have seen, does vary in the air, although through only small limits, hence they cannot be united to form a compound.

(4.) The proportion by weight in which oxygen and nitrogen are present in air, bears no simple relation to the atomic weights of these elements.

(5.) When air is dissolved in water, the oxygen and nitrogen dissolve as from a simple mixture of these gases, in accordance to the law of partial pressures (see page 127).

(6.) The oxygen and nitrogen can be partially separated, by taking advantage of the different rates of diffusion of these two gases (see Diffusion of Gases, page 80).

The various gases of the atmosphere are maintained in a state of uniform admixture, in spite of their widely different densities, by the operation of two causes: first, air currents, which effect the rapid removal of large masses of air from place to place; and, second, their own molecular movements, which bring about the phenomena *of gaseous diffusion.*

**Suspended Impurities in the Atmosphere.**—Besides t gaseous constituents of the air, there is always present a certa quantity of suspended matter, both liquid and solid. The exi ence of this suspended matter in the air, can be rendered evide from the fact, that these minute particles are capable of reflecti light; if, therefore, a strong beam of light be passed through darkened room, the track of the beam is distinctly visible, account of its being reflected from innumerable particles floati about in the air, many of them appearing quite large. Pasteur h shown, that this suspended matter can be removed by filtrati through cotton wool.* Tyndall also has shown, that in und turbed air the suspended matter settles in the course of a f hours, leaving the air almost entirely free from this impuri For this purpose the floor of a large oblong glass box w smeared over with glycerine. The box, after being hermetica closed, was then allowed to stand for twenty-four hours, duri which time the suspended matter subsided, and adhered to t glycerine. When a beam of light is allowed to pass through that has been thus freed from suspended matter, there bei nothing present to reflect the light, the beam cannot be see its track will be evident in the air of the room as it enters a leaves the box, but within the box it will be invisible (as rep sented in Fig. 52). To air in which a beam of light is in this w invisible, Tyndall has applied the term "optically pure."

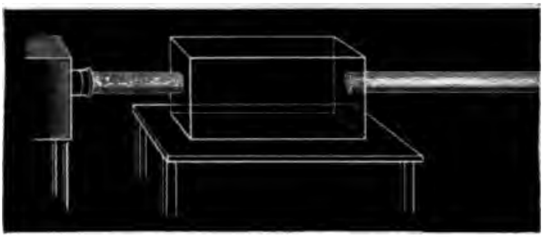


FIG. 52.

The suspended matters are partly mineral and partly orga Of the mineral matters, sodium chloride and certain sulpha are present in greatest quantity. These are thrown into the in the sea-spray, and as the small globules of water evapor

---

[*] See Experiments 317 to 325, "Chemical Lecture Experiments."

ave minute residual particles of saline matter, which, riven by the wind, remain floating in the atmosphere. It very rarely, even at far inland places in Europe, that spec ic examination fails to detect the presence of sodium com in the air. In the air of islands, such as England, it is bsent. Sulphates are also produced by the oxidation and stion of sulphuretted compounds; the amount of these, there greatly increased in the neighbourhood of towns.

organic suspended matter of the air has of late years been the subject of extended research. Pasteur has shown that st these organic substances are the germs and organisms produce fermentation, putrefaction, and disease. Putrescible nces, such as milk, urine, flesh, &c., if themselves carefully rom all such germs, may be preserved unchanged, for ap ly any length of time, in air that has been deprived of all ded matter. It is highly probable that the salubrity or ise of different places, is associated with the nature and t of the organic matter in the air, and it is certain that organisms play a most important part in relation to the life alth of man. The feelings of lassitude and headache, which from the prolonged breathing of the air of rooms containing people, are brought about more by the poisonous effects of ganic emanations evolved during respiration, than by any ation in the supply of oxygen, or increase in the proportion bon dioxide in the air. The well-known and unpleasant that is perceived on first entering a crowded room, is also the same cause, and it has been shown that the moisture condenses from such an atmosphere upon a cold object, if ved for a short time, rapidly becomes putrescent, owing to composition of this organic matter.

presence of suspended matter in the air, appears to exert a kable influence upon the formation and character of fogs. has shown that those conditions which result in the forma f a fog in ordinary air, are incapable of producing that effect that has been freed from suspended matter. It would appear he suspended particles act as innumerable points, or nuclei, facilitate the deposition of moisture, much in the same way crystallisation of a salt, from its solution, is known to start any minute particles of foreign matter that may be floating in quid.

height to which the atmosphere extends has been variously estimated. From observations of the flight of meteorites, it a pears that even at a height of seventy to seventy-five miles t air still has a sensible degree of density. The air being ela and subject to the law of gravitation, its density, which is grea at the earth's surface, rapidly diminishes as the altitude increas thus, at about three and a half miles the density is only one-h and at seven miles one-third, of that which obtains at the sea-lev From a consideration of the physical properties of gases, there every reason to believe, that in an extremely attenuated conditi the atmosphere extends far into space, and it has been calculat that the pressure exerted by our atmosphere upon the surface the moon, is equal to about 1 mm. of mercury.

The density of the atmosphere varies at different points of th earth's surface, and at the same point at different times. Th pressure exerted by the atmosphere is measured by the heig of a column of mercury which it is capable of supporting, th instrument employed for the purpose being called the baromete At the sea-level in the latitude of London, the average weight o the atmosphere is equal to that of a column of mercury 760 mm at 0°, and this is taken as the *standard pressure of the atmosphere.*

# CHAPTER VII

## *COMPOUNDS OF NITROGEN AND HYDROGEN*

THREE compounds of nitrogen with hydrogen have been prepared, namely:—

| | |
|---|---|
| Ammonia . . . . . | $NH_3$. |
| Hydrazine . . . . . | $N_2H_4$ or $(NH_2)_2$. |
| Hydrazoic acid . . . . | $N_3H$ or $HN_3$. |

### AMMONIA.

Formula, $NH_3$. Molecular weight = 17. Density = 8.5.

**History.**—Salts of ammonia, and also the aqueous solution, were known to the alchemists. It was termed by Glauber, *spiritus volatilis salis armoniaci*, being obtained by the action of an alkali upon *sal-armoniacum*. Subsequently, when ammonia was obtained by the destructive distillation of such refuse as hoofs and horns of animals, the name *spirits of hartshorn* was applied to it. The actual discovery of gaseous ammonia was made by Priestley (1774), when he collected the gas, evolved by the action of lime upon sal-ammoniac, by means of his mercurial pneumatic trough. Priestley named the gas *alkaline air*.

**Occurrence.**—In combination as carbonate of ammonia it is present in small quantities in the air, derived by the decay of nitrogenous animal and vegetable matter. As nitrate and nitrite it is found in rain water. It is evolved, along with boric acid, from the fumaroles of Tuscany (see Boric Acid), and is found as chloride and sulphate in the vicinity of active volcanoes.

**Modes of Formation.**—(1.) Ammonia can be synthetically produced, by submitting a mixture of nitrogen and hydrogen to the influence of the silent electric discharge (Donkin). The amount of ammonia so obtained, however, is extremely small, and can best be shown by passing the gases, as they issue from the "ozone tube," through a cylinder containing a small quantity of Nessler's solution.* In a short time the solution will begin to show a yellowish brown colour, indicating the presence of traces of ammonia.

(2.) Ammonia may be prepared by gently heating any of its salts, with either of the caustic alkalies, potash or soda, or with slaked lime. The salt most commonly employed is the chloride. When this is mixed with an excess of slaked lime, and the mixture gently heated in a flask, ammonia is evolved, and calcium chloride and water are formed—

$$2NH_4Cl + CaH_2O_2 = CaCl_2 + 2H_2O + 2NH_3.$$

The gas may be dried by being passed through a cylinder containing lumps of quicklime,† and may then be collected either by upward displacement, or in the mercurial trough. On account of its extreme solubility it cannot be collected over water.

(3.) Ammonia is formed by the action of nascent hydrogen upon salts of nitrous and nitric acid, thus—

$$NaNO_3 + 4H_2 = NaHO + 2H_2O + NH_3.$$

This method is often made use of, in the quantitative estimation of nitrates in drinking water.

(4.) When nitrogenous organic matter is subjected to destructive distillation, that is, strongly heated out of contact with air, ammonia is formed: hence when coal, which usually contains about 2 per cent. of nitrogen, is distilled in the process of the manufacture of ordinary illuminating gas, one of the products of the decomposition is ammonia. The "ammoniacal liquor" of the gas works, is the source of all ammonia salts at the present day. The liquor is boiled with milk of lime, and the ammonia thus expelled is absorbed by sulphuric acid. The ammonium sulphate so obtained is evaporated to dryness, and purified by recrystallisation.

**Properties.**—Ammonia is a colourless gas, having a powerfully pungent smell, and a strong caustic taste. It is lighter than air, its density being 0.589 (air = 1). Ammonia possesses the property of alkalinity in a very high degree; it turns red litmus blue, and yellow turmeric brown. The gas is unable to support combustion, s irrespirable. Under ordinary conditions ammonia is not ustible, but if the air be heated, or if the amount of oxygen be ased, the gas will then burn with a flame of a characteristic -ochre colour. This behaviour of ammonia as regards com- ility, is most conveniently ated by means of the ap- s shown in Fig. 53. A of the gas, obtained by heating a quantity of the aqueous solution in a lask, is delivered through which is surrounded by r glass tube. Through k which carries this tube d tube passes, through a supply of oxygen can sed. On applying a taper to the jet of am- s it issues from the tube, e noticed that the gas n the heated air round e of the taper, but is o continue burning when r is withdrawn. If now stream of oxygen be d into the annular space the two tubes, the am- eadily ignites, and continues to burn with its character- ne. On cutting off the supply of oxygen, the flame of the ammonia languishes and dies out.

---

* A solution of mercuric iodide in potassium iodide, rendered alkaline with potassium hydroxide.

† The usual desiccating agents, namely, sulphuric acid, or phosphorus pentoxide, are inadmissible in the case of ammonia, as this gas at once unites with such compounds.

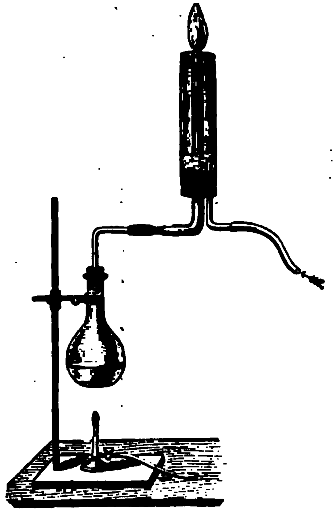


FIG. 53.

onia is extremely soluble in water; 1 c.c. of water at 0° C., the standard pressure, dissolves 1148 c.c. of ammonia, ed at 0° C. and 760 mm. The solubility rapidly decreases emperature rises, as will be seen by the following table:—

| 1 c.c. of Water at 760 mm. Dissolves | Grammes, $NH_3$. | c.c. at 0° C. and 760 mm. |
|---|---|---|
| At 0° | 0.875 | 1148 |
| „ 8° | 0.713 | 923 |
| „ 16° | 0.582 | 764 |
| „ 30° | 0.403 | 529 |
| „ 50° | 0.229 | 306 |

When a solution of ammonia is heated, the gas is rapidly evolved, and at the boiling temperature the whole of it is given up.

The great solubility of this gas in water may be shown by filling a large bolt-head flask with ammonia by displacement, the flask being closed by means of a cork through which a long tube passes, as shown in Fig. 54. On removing the cork from the end of the tube, water slowly rises until it reaches the top, and as soon as the first drops enter the globe the absorption proceeds with great rapidity, the water being forced up the tube in the form of a fountain, which continues until the flask is filled.

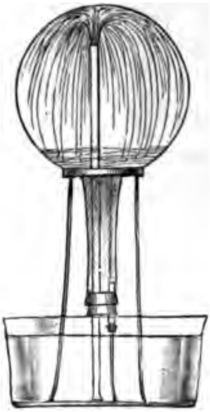


FIG. 54.

Commercial *liquor ammoniæ* is prepared by passing ammonia gas into water; the strongest solution has a specific gravity of 0.882 at 15°, and contains 35 per cent. of ammonia. During the process of solution heat is liberated, and when the gas is again expelled, the same amount of heat is reabsorbed. If a rapid stream of air be driven through a quantity of strong ammonia solution, contained in a glass flask, the ammonia gas is quickly expelled; and if the flask be placed upon a wooden block, as seen in Fig. 55, upon which a few drops of water have been poured, it will be found that after a few moments the flask will have become firmly frozen to the block. By the rapid evaporation of ammonia in this way, it is possible to lower the temperature to $-40°$ C.

Ammonia is an easily liquefiable gas; thus at 15.5° it requires a pressure of 6.9 atmospheres, and at 0° only 4.2 atmospheres, in order to liquefy it. The gas was first liquefied by Faraday (1823), by heating in one limb of a closed and bent glass tube (see Fig. 2), a quantity of a compound of ammonia with silver chloride, the other limb of the tube being immersed in a freezing mixture. The experiment may be made in a tube constructed as seen in Fig. 56. The wide limb is nearly filled with dry precipitated silver chloride, which has been saturated with ammonia gas. This compound melts at about 38°, and at a somewhat higher temperature it gives up its ammonia. If the narrow limb of the tube be immersed in a freezing mixture while the compound is being heated, the com-l influence of the cold, and the pressure exerted by the ed ammonia, will cause the gas to liquefy and collect in the portion of the tube. On removing the tube from the freezing ure, and allowing the other end to cool, the liquid ammonia boil off, and be reabsorbed by the silver chloride, reforming original compound.

quid ammonia is easily obtained in larger quantity, by passing gas through a glass tube immersed in a bath of solid carbonic and ether. Liquid ammonia is a colourless, mobile, and ily refracting liquid, boiling at −33.7°, and having a specific rity at 0° of 0.6234. When cooled below −75° it solidifies to a s of white crystals.

iquid ammonia dissolves the metals sodium and potassium, the ition in each case being of an intense blue colour. On the poration of the liquid, the metal is deposited unchanged.

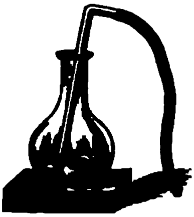


FIG. 55.

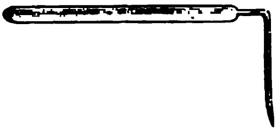


FIG. 56.

During the evaporation of liquid ammonia, boiling as it does at low a temperature as −33.7°, a rapid absorption of heat takes ce, and as this substance is so easily obtained it was one of the liest liquids employed for the artificial production of ice. Various making machines have been invented by M. Carré, in which reduction of temperature required is obtained by the evapora- of liquid ammonia.

mmonia is decomposed into its elements at a temperature ow a red heat. In this decomposition, two volumes of ammonia e one volume of nitrogen, and three volumes of hydrogen. The eous products, therefore, obtained by passing ammonia through d hot tube, are inflammable. In the same way, when electric rks are passed through ammonia, the gas is resolved into its stituents. By performing this experiment upon a measured ime of ammonia, confined in a eudiometer over mercury, it will be found, that after the passage of the sparks for a short time, and the readjustment of the levels of mercury, the original volume of the gas has been doubled.

The fact that the hydrogen and nitrogen are present in ammonia in the proportion of three volumes of hydrogen to one of nitrogen, can be shown by taking advantage of the fact that ammonia is decomposed by chlorine, the latter combining with the hydrogen to form hydrochloric acid, and the nitrogen being set free. This is effected by means of the apparatus shown in Fig. 57. The long glass tube, divided into three equal divisions, is filled with chlorine and closed by a cork carrying a small dropping funnel. A few cubic centimetres of strong aqueous ammonia are poured into the funnel and allowed to enter the tube drop by drop. As the first two or three drops fall into the chlorine, it will be seen that the combination is attended with a feeble flash of light, and fumes of ammonium chloride are formed. When the reaction is complete, the whole of the chlorine will have combined with hydrogen, derived from the ammonia, to form hydrochloric acid, and this in its turn will combine with the excess of ammonia added, forming ammonium chloride. This substance dissolves in the water. A small quantity of dilute sulphuric acid is next introduced by means of the dropping funnel in order to absorb the remaining excess of ammonia. The atmospheric pressure is then once more restored by attaching to the funnel a bent tube, dipping into a beaker of water as shown in the figure, and when the water is allowed to enter, it will be found to flow into the tube until it reaches the second graduation. The gas which is left, and which occupies one of the divisions of the tube, is found on examination to be nitrogen. This one measure of nitrogen, therefore, has been eliminated from that amount of ammonia which has been decomposed by the chlorine, with which the tube was originally filled. Now chlorine combines with its own volume of hydrogen, therefore the volume

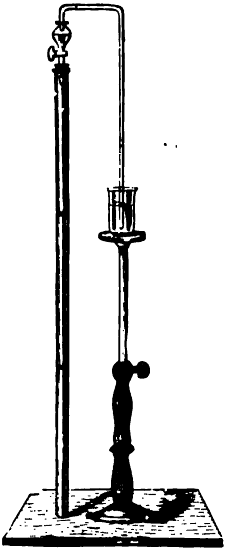


FIG. 57.

of hydrogen which was in combination with the one measure of nitrogen, is equal to the volume of chlorine contained in the tube, that is to say, it was three measures. We have, therefore, one measure of nitrogen and three measures of hydrogen, or, in other words, ammonia is a combination of nitrogen and hydrogen in the proportion of one volume of nitrogen to three volumes of hydrogen.

Ammonia combines directly with acids forming salts, known as ammonium salts, in which the nitrogen functions as a pentad element; thus with hydrochloric and sulphuric acids it forms respectively ammonium chloride and ammonium sulphate—

$$NH_3 + HCl = (NH_4)Cl.$$
$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$

(The ammonium salts will be described with the compounds of the alkali metals.)

**Hydrazine**, $NH_2{\cdot}NH_2$ or $N_2H_4$.—This compound was first prepared by Curtius (1887). It is obtained by heating together in a sealed tube, to a temperature of 170°, hydrazine hydrate, $N_2H_4,H_2O$, and barium monoxide. Under these circumstances the barium oxide takes up the water from the hydrazine hydrate, according to the equation—

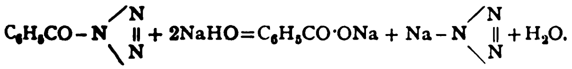
$$BaO + N_2H_4H_2O = Ba(HO)_2 + N_2H_4.$$

When the tube is opened, the gaseous hydrazine, which is under considerable pressure, rushes out of the tube, forming dense fumes in contact with the atmospheric moisture, with which it combines with great readiness.

**Hydrazine Hydrate**, $N_2H_4H_2O$.—The compound formed by the combination of hydrazine with water is obtained by distilling hydrazine sulphate, $N_2H_4H_2SO_4$, with an aqueous solution of potassium hydroxide (caustic potash) in a vessel of silver. It is a colourless, fuming, powerfully corrosive liquid, which boils at 118.5°. It attacks glass, corks, and indiarubber, and can only be prepared in vessels of silver or platinum which are screwed together at their junctions. With the halogen acids it forms two series of salts, in which either one or two molecules of the halogen acid are present; thus with hydrochloric acid we have—

| | |
|---|---|
| Hydrazine monohydrochloride . . . | $N_2H_4,HCl$. |
| Hydrazine dihydrochloride . . . . | $N_2H_4,2HCl$. |

**Hydrazoic Acid**, $HN_3$.—Discovered by Curtius (1890). The sodium salt is prepared by boiling benzoylazo-imide with sodium hydroxide, when sodium benzoate and sodium hydrazoate are formed, thus—



$$C_6H_5CO-N\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right. + 2NaHO = C_6H_5CO{\cdot}ONa + Na-N\left\langle\begin{matrix}N\\ \|\\ N\end{matrix}\right. + H_2O.$$

It is also produced when sodamide (obtained by heating sodium in dry ammonia gas) is heated to 200° in a stream of nitrous oxide—

$$2NH_2Na + N_2O = NaN_3 + NaHO + NH_3.$$

The sodium hydrazoate so obtained is then gently warmed with dilute sulphuric acid, when sodium sulphate and hydrazoic acid are formed, thus—

$$2NaN_3 + H_2SO_4 = Na_2SO_4 + 2HN_3.$$

**Properties.**—This compound is a colourless gas, possessing a most unpleasant and powerfully penetrating odour. If inhaled, even when largely diluted with air, it exerts an irritating action upon the mucous membrane. As its name denotes it is an acid substance, and in many of its properties it strongly resembles the halogen acids. The gas is extremely soluble in water, and forms a strongly acid liquid which smells of the gas. This solution when boiled, finally assumes a definite strength, and yields on distillation an aqueous acid of constant composition, in this respect resembling aqueous hydrochloric acid, *q.v.*

In its constitution this acid may be compared with hydrocyanic acid, and with the halogen acids—

$$H(N_3);\ H(CN);\ H(Cl);\ H(Br),$$

in which the radical cyanogen (CN), or the halogen elements, Cl and Br, are replaced by the group consisting of three nitrogen atoms.

When a solution of hydrazoic acid is added to a solution of silver nitrate, a white precipitate of silver hydrazoate is formed, strongly resembling silver cyanide and silver chloride. This silver salt, however, is not acted upon by light in the way the chloride is, and it differs also in being extremely explosive. A minute quantity of the compound, when touched with a hot wire, detonates violently.

When gaseous hydrazoic acid is mixed with gaseous ammonia, dense white fumes are formed, consisting of ammonium hydrazoate. These two hydrides of nitrogen, apparently so similar, but in reality so widely different, unite to form the ammonium salt, just as gaseous hydrochloric acid and ammonia combine to form ammonium chloride, thus—

$$NH_3 + H(N_3) = NH_4(N_3).$$
$$NH_3 + HCl = NH_4Cl.$$

The *alkaline* hydride of nitrogen, ammonia, combines with the *acid* hydride of nitrogen, hydrazoic acid, and forms the salt ammonium hydrazoate $NH_4N_3$ or $N_4H_4$.

## HYDROXYLAMINE.

Formula, $NH_2(OH)$.

Discovered by Lossen in 1865.

**Modes of Formation.**—(1.) By the action of nascent hydrogen upon nitric oxide, nitric acid, or certain nitrates—

$$2NO + 3H_2 = 2NH_2(OH).$$
$$HNO_3 + 3H_2 = 2H_2O + NH_2(OH).$$

The nascent hydrogen is evolved from tin and hydrochloric acid, and a stream of nitric oxide passed through the mixture. The drochloride of hydroxylamine is thus obtained. This is purified first passing a stream of sulphuretted hydrogen through the lution. The tin is thus precipitated as sulphide, and is removed y filtration. The filtered solution is then evaporated to dryness, and e hydrochloride of hydroxylamine is dissolved out of the residue y means of absolute alcohol, in which solvent ammonium chloride s only very slightly soluble. The alcohol is then distilled off, and he residue is converted into the sulphate by being treated with the equisite quantity of sulphuric acid. Hydroxylamine itself, in queous solution, is obtained from the sulphate by the addition of baryta-water.

(2.) By boiling potassium hydroxylamine-disulphonate with water for several hours—

$$2N(OH)(SO_3K)_2 + 4H_2O = (NH_3OH)_2SO_4 + 2K_2SO_4 + H_2SO_4.$$

The potassium sulphate is removed by crystallisation.

**Properties.**—Hydroxylamine is known only in aqueous solution. The solution is colourless, and has an alkaline character. When the solution is distilled the substance is partially decomposed. The solution is a powerful reducing agent: it precipitates gold and mercury from their solutions, and reduces cupric salts, throwing down the red cuprous oxide on being boiled.

Hydroxylamine is a base, and may be regarded as ammonia, in which one of the hydrogen atoms has been replaced by the monad group *hydroxyl* (OH). Its salts, like those of ammonia, are formed by direct union with an acid, without the elimination of water.

$$NH_2OH + HCl = NH_3OHCl \text{ (or } NH_2OH,HCl).$$
$$2NH_2OH + H_2SO_4 = (NH_3OH)_2SO_4 \text{ (or } 2NH_2OH,H_2SO_4).$$

The salts of hydroxylamine all decompose on the application of heat, with a more or less sudden and violent evolution of gas; thus the nitrate breaks up with almost explosive violence into nitric oxide and water—

$$NH_2OH{\cdot}HNO_3 = 2NO + 2H_2O.$$

### AMMON-SULPHONATES.

These compounds may be regarded as derived from ammonia, by the gradual replacement of the hydrogen by the group $SO_3H$ or $SO_2OH$.

| | |
|---|---|
| Ammon-sulphonic acid . . . | $NH_2(SO_3H)$. |
| Ammon-disulphonic acid . . . | $NH(SO_3H)_2$. |
| Ammon-trisulphonic acid. . . | $N(SO_3H)_3$. |

Potassium ammon-trisulphonate is precipitated as a crystalline salt w excess of a solution of potassium sulphite is added to a solution of potas nitrite—

$$3K_2SO_3 + KNO_2 + 2H_2O = 4KHO + N(SO_3K)_3.$$

Prolonged boiling with water converts it first into the ammon-disulphonat

$$N(SO_3K)_3 + H_2O = NH(SO_3K)_2 + HKSO_4,$$

and finally into ammon-sulphonate—

$$NH(SO_3K)_2 + H_2O = NH_2(SO_3K) + HKSO_4.$$

Ammon-sulphonic acid is a stable crystalline body; the other two aci only known in their salts.

When an ice-cold solution of sodium nitrite is added to hydrogen s sulphite, a compound is obtained which may be regarded as derived ammon-trisulphonic acid by the replacement of one of the groups, SO hydroxyl, OH—

$$NaNO_2 + 2NaHSO_3 = N(OH)(SO_3Na)_2 + NaHO.$$

On the addition of a saturated solution of potassium chloride, in the co sodium salt is converted into the potassium salt, which slowly crystallise the solution, with two molecules of water, $N(OH)(SO_3K)_2.2H_2O$.

This potassium hydroxylamine disulphonate is an unstable compoun on boiling with water the two $SO_3K$ groups are replaced by hydrogen, f first potassium hydroxylamine monosulphonate, $NH(OH)SO_3K$; and hydroxylamine, $NH_2OH$.

## COMPOUNDS OF NITROGEN WITH THE HALOGEN ELEM

**Nitrogen Trichloride**, $NCl_3$.—This compound was discovered by I (1811). Its true composition was proved by Gattermann (1888).

**Mode of Formation.**—Nitrogen trichloride is obtained by the act chlorine upon ammonium chloride—

$$NH_4Cl + 3Cl_2 = NCl_3 + 4HCl.$$

When a solution of ammonium chloride is electrolysed, the chlorine, w evolved at the positive electrode, acts upon the ammonium chloride, formi trichloride of nitrogen.*

**Properties.**—Nitrogen trichloride is a thin oily liquid, of a pale colour, and having a specific gravity of 1.65. It is very volatile, and unpleasant pungent smell, the vapour being extremely irritating to the ey is the most dangerously explosive compound known, and when su heated, or brought into contact with grease, turpentine, or phosphorus it explodes. It also explodes on exposure to sunlight. At a temperature it may be distilled, but the operation is one of the utmost danger. Ni trichloride is decomposed by ammonia, forming ammonium chloride an ence in the preparation of nitrogen by the action of chlorine upon he presence of an excess of ammonia prevents the formation of this ompound.

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* See "Chemical Lecture Experiments," No. 286.

**Tribromide**, $NBr_3$.—When potassium bromide is added to nitro- :ide beneath water, a red, oily, highly explosive substance is lieved to be the tribromide of nitrogen.

**Iodide**, $NHI_2$.—When strong aqueous ammonia is added to odine, a brown-coloured powder is formed which has violently operties.* Also when alcoholic solutions of iodine and of ammonia brown and highly explosive compound is produced. The com- enerally been called iodide of nitrogen, or nitrogen iodide, but its sition has been a matter of dispute, and it is still an unsettled point compound obtained by the different methods is identical or not. who first prepared the substance, believed it to have the composi- d this view was held by Gay-Lussac and others. Gladstone and lered that the substance contained one atom of hydrogen, and that $NHI_2$ expressed the composition. The recent investigations of 3) prove indubitably that the compound obtained by the addition of aqueous ammonia to a concentrated solution of iodine in odide, has the composition $NHI_2$. Whether under different l conditions other compounds are capable of formation, in which or less of the hydrogen has been substituted by iodine, such as $_3$I, still remains to be proved. The reaction by which the com- duced may be thus expressed—

$$3NH_3 + 2I_2 = NHI_2 + 2NH_4I.$$

s.—Nitrogen iodide is a dark chocolate-brown powder. When be handled without much risk of explosion, although it has been xplode even under water. When dry, the substance is extremely e shock caused by the tread of a fly upon it, is more than sufficient ; even falling dust particles will sometimes cause it to explode. To explosive nature, a small quantity of the wet substance should be ry spontaneously upon a wooden block: in a few hours it will have ciently dry to readily explode if lightly touched by a feather.

ogen iodide is placed in dilute aqueous ammonia, and exposed to it is decomposed, and bubbles of nitrogen are seen escaping from d.

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[*] Experiment 287.

# CHAPTER VIII

## *CARBON*

**Symbol, C. Atomic weight = 11.97.**

**Occurrence.**—This element is capable of assuming thre
tropic forms, and it occurs free in nature in each of these mo
tions, viz., diamond, graphite, and charcoal.

In combination with oxygen, carbon occurs in carbon dio
gas which is present in the air, being a constant product o
bustion and respiration. In combination with hydrogen it
as marsh gas. Carbon is a constituent of all the natura
bonates, such as limestone, dolomite, &c., which form an imp
fraction of the earth's crust, and it is also an essential cons
of all organic substances.

### DIAMOND.

**Occurrence.**—This substance has been known and prize
the remotest antiquity. It is found in various parts of
mostly in river gravels and superficial deposits, in Brazil,
Africa, Australia, and various parts of the United States.
diamond has also recently been obtained from extra-ter
sources. In a meteorite which fell in Russia on Septeml
1886, carbon was found, partly as amorphous, and partly a
mantine carbon.

The diamond form of carbon is found of various colours ;
times it is dark grey, or even black, stones of these colours
known as carbonado and bort. The former of these is ext
hard, and is of great value for use in rock-boring and
instruments. Bort is used in the crushed condition by lap
for grinding and polishing.

Occasionally the diamond is found coloured blue, or
green, by traces of foreign materials. Some of these co

are of great value as gems: the well-known "Hope" nd, a stone weighing 44½ carats, has a fine sapphire colour. e origin of the diamond is unknown, although many theories been put forward to explain its formation. Newton's famous estion that diamond was "an unctuous substance coagulated," based upon its remarkably high refractive index. The cellular cture which is sometimes to be seen in the ash that is left when diamond is burnt, seems to indicate that it is of vegetable in.

**odes of Formation.**—Innumerable attempts have been made ffect the crystallisation of carbon in the adamantine form; but le it is readily possible to convert this variety of carbon into its tropes graphite and charcoal, the transformation of these back in to the diamond, is a problem that is beset with the greatest iculties. Moissan has recently shown* that the carbon which apable of being dissolved in molten iron, and which is usually osited in the graphitic form on cooling, can, under certain ditions, be caused to take up the adamantine form.

y raising the temperature of the iron to about 3000° by means n electric furnace, and then suddenly cooling the molten mass plunging the crucible into water or molten lead, until the cooled l solidified surface is at a dull red heat, an enormous pressure is ught to bear upon the interior and still liquid portion. Under se circumstances, a part of the carbon which is deposited by the vly cooling mass, was found by Moissan to be in the adamantine n. On dissolving the iron in hydrochloric acid, amongst the bonaceous residue were found fragments having a specific vity between 3.0 and 3.5, and sufficiently hard to scratch ruby. ne of the fragments were the black or carbonado variety, while ers were transparent. On combustion in oxygen, Moissan ved that these were really carbon in the diamond form.

**roperties.**—The diamond in its purest condition is a colourless stalline substance. Its crystalline forms belong to the cubic tem, and appear to some extent to be characteristic of the lity in which the element occurs. It is extremely hard, and lerately brittle. When struck with a hammer, the diamond not y splits along its cleavage-planes, but also in other directions, a conchoidal fracture. It does not conduct electricity. The cific gravity of diamond varies slightly in different specimens, the mean being about 3.5. Its refractive index is higher tha of any other substance, and it is this property which giv peculiar beauty and brilliancy to the cut stone.

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* *Comptes Rendus de l'Académie des Sciences*, vol. cxvi. p. 218.

The value of diamond as a gem, depends largely upon its co lessness, except in the case of those rare instances where colour is quite definite and also pleasing, such as distinct red; or green.

When diamond is strongly heated it becomes black, and creases in bulk, being converted into a substance having properties of graphite. Lavoisier (1772) was the first to that the diamond was a combustible body, and that it yie carbon dioxide. Davy (1814) showed that carbon dioxide was only product of its combustion, and pro that diamond was pure carbon.

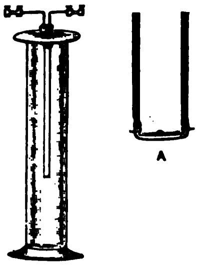

Fig. 58.

The combustion of diamond in oxy may readily be accomplished by means the apparatus shown in Fig. 58. A fragm of diamond is supported upon a small gut of platinum foil, which bridges across tw stout copper wires, A. These wires pa through a cork in a perforated glass plat and are lowered into a cylinder of oxyge By the passage of an electric current, th little platinum boat can be strongly heated when the diamond will become ignited, an continue to burn brilliantly in the oxygen, with the formation o carbon dioxide. The ash, which is always left after a diamon has been burnt, varies from 0.2 to 0.05 per cent. of the ston It is found usually to contain ferric oxide and silica.

## GRAPHITE.

**Occurrence.**—This second allotrope of carbon is much mo plentiful in nature than the first. It is found in large quantiti in Siberia, Ceylon, and various parts of India. In England th chief source of graphite has been the mines at Borrowdale, i Cumberland; this supply is now practically exhausted. Eno mous quantities of very pure graphite are now obtained from th Eureka Black-Lead Mines, in California. Graphite also occu in many specimens of meteoric iron.

**Mode of Formation.**—Molten iron, especially when it contai on, is capable of dissolving a considerable amount of carbon, ch, on cooling, is deposited in the form of black shining crystals graphite. Occasionally considerable quantities of graphite are d deposited in this way in iron-smelting furnaces, to which the e "kish" has been applied.

**roperties.**—Graphite is a soft, shiny, greyish-black substance, ch is smooth and soapy to the touch. It is usually found in pact laminated masses, but sometimes crystallised in six-sided tes. Its specific gravity varies in different specimens, aver g about 2.5. Graphite is a good conductor of both heat and tricity.

When strongly heated in oxygen, graphite takes fire and burns, ing carbon dioxide, and leaving an ash consisting of silica, mina, and oxide of iron. Graphite has been found by Regnault contain, usually, traces of hydrogen. Graphite is employed for manufacture of ordinary lead pencils; for, on account of its soft s, it leaves a black mark upon paper when drawn across it. r the purposes of the pencil manufacture the natural graphite is und to powder, and carefully washed free from gritty matter. is then mixed with the finest washed clay, and the pasty mass is ced by hydraulic pressure through perforated plates. The name graphite," from the Greek *to write*, is given to this substance on count of its use for this purpose. It was formerly supposed at this material contained lead, hence the names *black-lead* and *mbago*.

Graphite is largely employed, on account of its refractoriness, r the manufacture of the so-called plumbago crucibles, which nsist of fireclay, mixed with finely-ground graphite.

Other uses to which graphite is put, are for glazing or polishing npowder, especially the larger grained varieties; as a lubricant r machinery, where oil is inadmissible on account of high tem rature; for electrotyping processes, and also as a coating for onwork, to prevent rusting.

## AMORPHOUS CARBON.

This non-crystalline form of carbon, may be obtained by the composition of a great variety of carbon compounds, by the ocess known as destructive distillation. The carbon so obtained ffers very much as regards its purity, according to the particular ganic compound used *for its preparation*. The commonest forms of amorphous carbon to be met with, are lampblack, or soot; ga carbon; coke; charcoal; animal charcoal, or bone-black. Ne of these substances is pure carbon; animal charcoal, for examp usually containing only about 10 per cent. of carbon.

**Lampblack.**—This substance is manufactured by burning s stances rich in carbon, and which burn with a smoky flame, ( turpentine, petroleum, or tar,) with a limited supply of air. Th smoke is passed into chambers in which are suspended co blankets, upon which the soot collects. This lampblack alw contains hydrogen, in the form of hydrocarbons. If the soot b heated to redness in a stream of chlorine, this hydrogen can b removed, and pure amorphous carbon will be left.

Lampblack is used for printers' ink, and for black paint.

**Gas Carbon.**—This form of carbon is obtained by the destru tive distillation of coal, in the manufacture of illuminating ga It remains in the retorts as an extremely hard deposit, lining th roof and sides. It is a very pure carbon, coming second to pu fied lampblack. Its specific gravity is about 2.35. Gas carbon i a good conductor of electricity, and is extensively used for th manufacture of carbon rods for the arc light.

**Coke.**—This substance differs from gas carbon, although it also is obtained in the process of coal distilling. It contains all the inorganic matter which constitutes the ash of the coal, and also small quantities of hydrogen, nitrogen, and oxygen. The average amount of carbon in coke is about 91 per cent.

**Charcoal.**—The purest form of charcoal is obtained by the carbonisation of pure white sugar, and the subsequent ignition of the charcoal in a stream of chlorine gas. Charcoal so obtained has a specific gravity of 1.57. Charcoal in a much less pure condition is manufactured from wood. The methods by which the carbonisation of wood is carried out are, broadly, of two kinds: first, those in which access of air is permitted to the burning material; and, second, those in which air is excluded.

The first of these, and the most ancient, is generally carried on in more primitive parts, where wood is plentiful. The wood is piled into mounds or stacks, which are built with some care. They are set on fire in the interior, by means of a lighted bundle of brushwood, which is introduced through a vertical opening or chimney, left for this purpose in the centre of the mound during its construction. The outside of the heap is covered with brushwood, and finally with turf, in order to regulate the access of air to the erior, and therefore to control the rate of combustion of the wood. ie object of the charcoal-burner is to carbonise the wood as wly as possible. In this process there is great liability to loss, y the too rapid combustion of the wood; and, in addition, it possses the disadvantage that the secondary products, such as the yroligneous acid, tar, &c., are entirely lost.

Various modifications have been introduced into the method of *aling* wood, as the process is termed, with a view to collect these roducts.

In the second general process of carbonising wood, the material s heated in ovens or retorts from the outside, no air being admitted o the wood. The operation is very similar to that employed in e destructive distillation of coal, in the manufacture of coal gas. these methods all the volatile and condensable products are llected; among these are water, pyroligneous acid, wood spirit, cetone, and fatty oils. The non-condensable products consist ainly of such gases as hydrogen, carbon monoxide, carbon di-ide, marsh gas, and acetylene.

**Animal Charcoal.**—Bone-black is obtained by the carbonisa-n of bones in iron retorts. This variety of charcoal is the least re of all the ordinary forms of amorphous carbon.

Bone contains only about 30 per cent. of organic matter, the her 70 per cent. consisting chiefly of calcium phosphate, assoated with small quantities of magnesium phosphate and calcium rbonate. It will be obvious, therefore, that as the carbon is rived from the organic matter, the amount of it in carbonised nes must be small. The average composition of animal charal is found to be—

| | |
|---|---|
| Carbon | 10.0 |
| Calcium phosphate | 88.0 |
| Other saline substances | 2.0 |
| | 100.0 |

lthough containing relatively so small an amount of carbon, nimal charcoal possesses many of the valuable properties of harcoal in a highly marked degree, owing to the fact that it conains its carbon disseminated throughout an extremely porous mass f calcium phosphate.

**Properties of Charcoal.**—Charcoal varies very considerably in its properties, depending *upon the* particular wood from which it is obtained, and the method by which it is prepared. Thus, cha coal obtained at 300° is a soft, brownish-black, very friable materi having an igniting point as low as 380°. On the other han charcoal prepared at very high temperatures is black and com paratively dense, and requires to be strongly heated in order t ignite it.

Under ordinary circumstances, charcoal burns in air without the formation of a flame, or the production of smoke. At high tem peratures, however, the combustion of charcoal is seen to be attended by a flame. This is probably accounted for by the fact, that as the temperature at which the combustion of carbon takes place is raised above 700°, the amount of carbon monoxide which is formed increases, and the carbon dioxide decreases.*

When charcoal is thrown upon water it floats, on account of the air which is enclosed within its pores. The specific gravity o charcoal when thus filled with air, varies from 0.106 (charcoal mad from the ash) to 0.203 (charcoal from the birch). If the air b withdrawn from charcoal it sinks in water, the average specifi gravity of charcoal itself being 1.5.

Ordinary charcoal is a bad conductor of electricity, but its con ductivity is greatly increased by strongly heating the charcoal i closed vessels.

Charcoal has the power of absorbing gases and vapours to remarkable extent: this power, which is exhibited to a differen degree by the various kinds of charcoal, is due to the porosity o the material, whereby it exposes a very large surface; and i belongs to a class of phenomena known as *surface action.*

If a fragment of charcoal, recently strongly heated to expel th air from its pores, be passed up into a cylinder of ammonia gas standing in a trough of mercury, the ammonia will be graduall absorbed by the charcoal, and the mercury will ascend in th cylinder. Saussure found, that recently heated beech-wood char coal was capable of absorbing ninety times its own volume o ammonia gas; while Hunter, by employing charcoal made fro cocoa-nut shell, found that 171.7 volumes of ammonia were absorbe by one volume of charcoal. The results of both of these experi ments show, that those gases are absorbed in the largest quantitie which are the most readily liquefiable. The gas so held by th charcoal, is in a highly condensed condition upon the surface o

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* Ernst (*Chemisches Repertorium*, vol. xvii. p. 2).

s mass. Probably in the case of easily liquefied gases
nmonia, sulphur dioxide, and others, the gases are par-
fied upon the surface of the charcoal. In this condensed
gas is more chemically active than under ordinary condi-
charcoal is therefore able to induce many striking com-
to take place. Thus, if charcoal be allowed to absorb
ınd dry hydrogen be then passed over it, the chlorine is
combining with the hydrogen even in the dark, with the
of hydrochloric acid. This chemical activity of gases,
ɔrbed by charcoal, is strikingly exemplified in the case
etted hydrogen. If a quantity of powdered charcoal,
been saturated with sulphuretted hydrogen, be brought
en, the rapid combination of the two gases is attended
development of so much heat, that the charcoal bursts
combustion. In the same way a mixture of air, with
per cent. of sulphuretted hydrogen, may be passed
rough a tube, about a metre in length, filled with char-
out a trace of sulphuretted hydrogen escaping at the
wing to this property, charcoal is largely employed
noxious gases, the atmospheric oxygen which is con-
the pores of the charcoal, oxidising these offensive and
compounds: thus sewer ventilators are often trapped
er of charcoal, which effectually arrests all bad-smelling

ıl also has the power of absorbing colouring-matters from
thus, if water which has been tinted with an organic
matter, be shaken up with powdered charcoal, and filtered,
ɔn will be found to be entirely decolourised. The variety
ıl which possesses this property in the highest degree, is
arcoal, or bone-black, and this substance is largely em-
many manufacturing processes, such as sugar refining,
ɔ remove all colouring-matter from the liquid.
ıl under ordinary conditions is unacted upon by the air
the temperature is raised, it enters into active combus-
ing carbon dioxide. In an extremely divided condition,
carbon is capable of combining spontaneously with the
the air, and with so much energy as to take fire.
The carbonaceous minerals that are included under the
*l*, are an impure form of carbon, containing compounds

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* "*Chemical Lecture* Experiments," 377–379.

of carbon with hydrogen and oxygen. Coal is the final result of series of decomposition changes, which have been undergone by vegetable matter of the remote past, the process having extended over long geological periods. During this prolonged process, a portion of the carbon and hydrogen is eliminated as marsh gas, and large quantities of this gas are found associated with, and occluded in, coal.

Broadly speaking, the numerous varieties of coal may be divided into *soft* or *bituminous*, and *hard* or *anthracitic*.

The former are employed for the manufacture of coal gas, and for ordinary domestic purposes; they burn with a smoky flame, and evolve large quantities of gases and volatile vapours, on combustion or distillation. Anthracite coal is much harder, ignites with more difficulty, and burns with the formation of very little flame or smoke. It contains a higher percentage of carbon, and gives out great heat on combustion, and is employed largely as a steam-coal.

The following table shows the average composition of coals from various sources, and the general difference between coals of the two main classes—

| | Locality. | Carbon. | Hydrogen. | Oxygen. | Nitrogen. | Sulphur. | Ash. | Water. | Coke. |
|---|---|---|---|---|---|---|---|---|---|
| Bituminous. | Northumberland | 81.41 | 5.83 | 7.90 | 2.05 | 0.74 | 2.07 | 1.35 | 66.70 |
| | Wales . . | 83.78 | 4.79 | 4.15 | 0.98 | 1.43 | 4.91 | ... | 72.60 |
| | Staffordshire . | 78.57 | 5.29 | 12.88 | 1.84 | 0.39 | 1.03 | 11.29 | 57.21 |
| Anthracite. | S. Wales . . | 92.56 | 3.33 | 2.53 | ... | ... | 1.58 | ... | ... |
| | Pennsylvania . | 90.45 | 2.43 | 2.45 | ... | ... | 4.6 | ... | ... |

# CHAPTER IX

## *CARBON COMPOUNDS*

THE compounds of the element carbon are so numerous, that it has been found convenient to constitute the study of these substances a separate branch of chemistry. In the early history of the science, it was believed that there were a large number of substances which could only be obtained as the product of living organisms. They were known to be elaborated by the action of life, or, as it was termed, the *vital force*, and it was believed, that owing to some inherent specific quality belonging to this vital force, the substances produced by its action were distinct from such substances as could be prepared by any laboratory processes. To denote this distinction, the term *organic* was applied to those things which were known to be the products of living organisms, and other compounds were distinguished as *inorganic* substances. This distinction received its deathblow in 1828, when Wöhler produced, by purely laboratory processes, one of the most typical of all organic compounds, namely, urea. The names "organic" and "inorganic" chemistry are still retained, but their old significance is entirely gone, as no distinction is to-day recognised between products elaborated by the action of life, and those which can be synthetically produced.

Speaking broadly, organic chemistry may be defined as the chemistry of the carbon compounds. This definition, however, includes such compounds as the oxides of carbon and all the carbonates, such as chalk, limestone, dolomite, &c., compounds which are more conveniently classed as inorganic. A more exact definition is the following:—*The chemistry of those compounds of carbon which contain in the molecule an atom of carbon, directly associated with either hydrogen, nitrogen, or another carbon atom.* This definition excludes all the carbon compounds which are by general consent regarded as belonging to the inorganic division of the science.

Three organic compounds will be briefly studied in the following chapters, namely, methane (marsh gas), $CH_4$; ethene (ethylene), $C_2H_4$; and acetylene, $C_2H_2$. These three compounds play an important part in our ordinary illuminating flames, and in coal gas.

## COMPOUNDS OF CARBON WITH OXYGEN.

Two oxides of carbon are known, both of which are colourless gases, viz. :—

| | |
|---|---|
| Carbon monoxide . . . . . | $CO$. |
| Carbon dioxide . . . . . . | $CO_2$. |

### CARBON MONOXIDE.

Formula, $CO$. Molecular weight = 27.96. Density = 13.98.

**Modes of Formation.**—(1.) Carbon monoxide is formed when carbon dioxide is passed over charcoal heated to bright redness—

$$CO_2 + C = 2CO.$$

The same result is obtained, when a slow stream of air or oxygen is passed over red-hot charcoal contained in a tube. The first action of the air, on coming in contact with the carbon, is to form carbon dioxide, which, passing over the remainder of the heated material, is deprived of a portion of its oxygen, according to the above equation. This operation goes on in an ordinary fire-grate; the air, on first gaining access to the burning coal or coke, causes the complete oxidation of a portion of the carbon, to carbon dioxide; and as this gas passes through the mass of red-hot carbon, it is reduced to the lower oxide, which either escapes with the other products of combustion, or becomes ignited and burns with a lambent bluish flame, such as may frequently be noticed upon the top of a "clear" fire.

(2.) When steam is passed over strongly heated carbon, a mixture of carbon monoxide and hydrogen is produced. This mixture, known as *water gas*, is employed in many manufacturing processes as a gaseous fuel—

$$H_2O + C = CO + H_2.$$

(3.) Carbon monoxide is also formed by the action of carbon dioxide upon red-hot iron—

$$4CO_2 + 3Fe = Fe_3O_4 + 4Co.$$

(4.) Or by strongly heating either carbon or iron with a carbonate, such as calcium carbonate, which is capable of yielding carbon dioxide, thus—

$$CaCO_3 + C = CaO + 2CO.$$
$$4CaCO_3 + 3Fe = Fe_3O_4 + 4CaO + 4CO.$$

(5.) Carbon monoxide is most conveniently prepared, by the decomposition of certain organic compounds by means of sulphuric acid. Thus, when formic acid, or a formate, is acted upon by sulphuric acid, the sulphuric acid withdraws the elements of water from the molecule of formic acid, and leaves carbon monoxide—

$$H{\cdot}COOH - H_2O = CO.$$

(6.) By a similar decomposition, oxalic acid yields a mixture of carbon monoxide and carbon dioxide in equal volumes—

$$C_2H_2O_4 - H_2O = CO_2 + CO.$$

The carbon dioxide is readily removed from the mixture, by passing the gases through a solution of sodium hydroxide (caustic soda), in which carbon dioxide is absorbed with the formation of sodium carbonate.

(7.) The method usually employed when carbon monoxide is required for experimental purposes, consists in heating a mixture of 1 part by weight of crystallised potassium ferrocyanide (yellow prussiate of potash) with ten parts of strong sulphuric acid in a capacious flask, when the following reaction takes place—

$$K_4FeC_6N_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO.$$

The six molecules of water required by the reaction, are derived partly from the acid employed, and partly from the salt, which contains three molecules of water of crystallisation.*

**Properties.**—Carbon monoxide is a colourless, tasteless gas, having a faint smell. It is only slightly soluble in water, its coefficient of absorption at 0° being 0.03287. It burns in the air with a characteristic pale blue flame, forming carbon dioxide—

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* "*Chemical Lecture* Experiments," 418-422.

$$2CO + O_2 = 2CO_2.$$

When mixed with half its own volume of oxygen, and inflamed, the mixture explodes with some violence.* If the two gases be confined in a eudiometer standing over mercury, and be rendered absolutely free from aqueous vapour by powerful desiccating agents, no explosion will take place upon the passage of an electric spark through the mixture. And in the same way if carbon monoxide, which has been deprived of all aqueous vapour, be burned from a jet in the air, and the jet be lowered into a cylinder containing air which has been similarly dried, the flame will be extinguished.

Carbon monoxide is an extremely poisonous gas: very small quantities present in the air, rapidly give rise to headache and giddiness, and if inhaled for a length of time, or if taken into the lungs in a less dilute condition, insensibility and death quickly follow. The deaths that have resulted from the use of unventilated fires—either of charcoal or coke, or in some cases of coal gas—in dwelling-rooms, have been due to the escape of this poisonous gas into the air. The extremely deadly nature of the *after-damp* resulting from a colliery explosion, is due to the presence of carbon monoxide in the carbon dioxide which is formed as a product of the combustion.

The poisonous action of this gas is due to its absorption by the blood, with the formation of a bright red compound, to which the name *carboxy-hæmoglobin* is applied. Blood so charged appears to be unable to fulfil its function of absorbing and distributing oxygen throughout the system. This carboxyhæmoglobin gives a characteristic absorption spectrum, which furnishes a ready method of detection, in cases of poisoning from the inhalation of carbon monoxide.

Carbon monoxide is one of the most difficultly liquefiable gases, its critical temperature being – 140°.

At high temperatures this gas is a powerful reducing agent, uniting with another atom of oxygen to form carbon dioxide. This fact is made use of in many metallurgical processes, for reducing the oxides of the metals to the metallic state.

---

[*] The rate at which the combustion is propagated throughout a mixture of carbon monoxide and oxygen, is much slower than through hydrogen and oxygen. Bunsen has estimated it at less than 1 metre per second.

Carbon monoxide is absorbed at ordinary temperatures by a solution of cuprous chloride, forming the compound $COCu_2Cl_2$.

At a temperature of boiling water, carbon monoxide is slowly absorbed by solid potassium hydroxide, with the formation of potassium formate—

$$KHO + CO = H \cdot COOK.$$

Carbon monoxide unites directly with chlorine, under the influence of sunlight, forming the compound known as *phosgene gas*, or carbonyl chloride—

$$CO + Cl_2 = COCl_2.$$

If the two gases are mixed in equal volumes, and kept in the dark, no action takes place, but on exposure to sunlight they combine, and the yellowish colour due to the chlorine will disappear. On opening the vessel in moist air, clouds of hydrochloric acid are formed, owing to the decomposition of carbonyl chloride by the moisture, according to the equation—

$$COCl_2 + H_2O = CO_2 + 2HCl.$$

Carbonyl chloride may be readily condensed to a liquid, its boiling-point being + 8°.

Carbon monoxide unites directly with certain metals, giving rise to compounds which possess some very remarkable properties, and to which the name *metallic carbonyls* has been applied by their discoverer.*

When carbon monoxide is allowed to stream slowly over metallic nickel (obtained by the reduction of nickel oxide in a stream of hydrogen), the gas is absorbed by the finely-divided metal, forming a compound having the composition $Ni(CO)_4$. If the issuing gas be passed through a cooled tube, the nickel carbonyl condenses to a colourless, mobile, highly refracting liquid, having a specific gravity at 0° of 1.356, and boiling at 43° under a pressure of 751 mm.†

Nickel carbonyl vapour burns with a luminous flame, which produces a black deposit of metallic nickel when a cold porcelain dish is depressed upon the flame. The gas is decomposed into nickel and carbon monoxide if passed through a hot glass tube, the nickel being deposited as a bright metallic mirror upon glass—

---

* Mond, *1890.*

† *See* "*Chemical Lecture Experiments*," 429–431.

$$Ni(CO)_4 = 4CO + Ni.$$

A similar compound of carbon monoxide and iron has also been obt having the composition $Fe(CO)_5$. Iron carbonyl is a pale-yellow, v liquid, boiling at 102.8° under a pressure of 749 mm. Its specific grav 18° is 1.4664. When heated to 180° the vapour is decomposed, iron deposited and carbon monoxide being evolved. This compound has been in iron cylinders in which the so-called *water gas* (a mixture of H and CC been stored under pressure for a length of time; it is also said to be pres minute quantities in coal gas.

## CARBON DIOXIDE.

Formula, $CO_2$. Molecular weight = 43.92. Density = 21.96.

**History.**—Van Helmont, in the seventeenth century, was the to distinguish between this gas and ordinary air: he observed th was formed during the processes of combustion and fermenta and he applied to it the name *gas sylvestre*. Black showed this gas was a constituent of what in his day were known as *mild alkalis* (alkaline carbonates), and on account of its bein combined, or fixed, in these substances, he named the gas *f air*. Lavoisier first proved its true chemical composition t that of an oxide of carbon.

**Occurrence.**—Carbon dioxide is a constant constituent of atmosphere, being present to the extent of about 3 volume 10,000 volumes of air. It is also found in solution in all spr water, which is sometimes so highly charged with this gas un pressure, that the water is effervescent, or "sparkling," from escape of the gas. Carbon dioxide is evolved in large quant from vents and fissures in the earth in volcanic districts. well-known Poison Valley in Java, which is an old volcanic cr and the Grotto del Cane near Naples, owe their peculiar perties to the discharge into them of large quantities of ca dioxide from such subterranean sources.

**Modes of Formation.**—(1.) Carbon dioxide* is produced w carbon is burnt with a free supply of air or oxygen—

$$C + O_2 = CO_2.$$

---

* Experiments on carbon dioxide, Nos. 383-417, "Chemical Lecture periments."

If an insufficient supply of oxygen be employed, carbon monoxide is produced at the same time.

(2.) When limestone, or chalk, is strongly heated, as in the process of burning lime, carbon dioxide is evolved in large quantities—

$$CaCO_3 = CaO + CO_2.$$

(3.) In the ordinary processes of fermentation, and during the decay of many organic substances, carbon dioxide is also formed. Thus, when sugar undergoes alcoholic fermentation by means of yeast, the sugar is converted into alcohol and carbon dioxide—

$$C_{12}H_{22}O_{11} + H_2O = 4C_2H_6O + 4CO_2.$$

(4.) Carbon dioxide is formed during the process of respiration; also by the combustion of all ordinary fuels, and of any compound containing carbon, such as candles, oils, gas, &c.

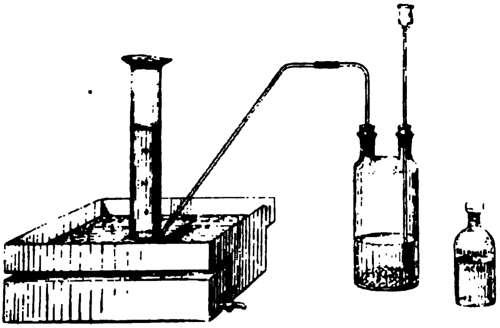

FIG. 59.

(5.) For experimental purposes, carbon dioxide is most readily obtained by the decomposition of a carbonate by means of a stronger acid. The effervescence that results from the action of tartaric acid upon sodium carbonate, in an ordinary Seidlitz powder, is due to the disengagement of this gas. The most convenient carbonate for the preparation of this gas is calcium carbonate, in one of its many naturally occurring forms, such as marble, limestone, or chalk. Fragments of marble are for this purpose placed in a two-necked bottle (*Fig. 59*), *with* a quantity of water, and strong hydrochloric acid is added by means of the funnel-tube. A rapid effervescence takes place owing to the elimination of the gas, and a solution of calcium chloride remains in the bottle—

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

If sulphuric acid be substituted for hydrochloric acid, the fragments of marble rapidly become coated with a crust of insoluble calcium sulphate, which soon prevents the further action of the acid, and therefore puts an end to the reaction: by employing finely powdered chalk, however, instead of lumps of calcium carbonate, this difficulty is obviated. This gas is largely manufactured from these materials.

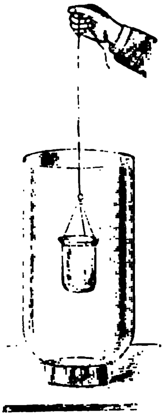

FIG. 60.

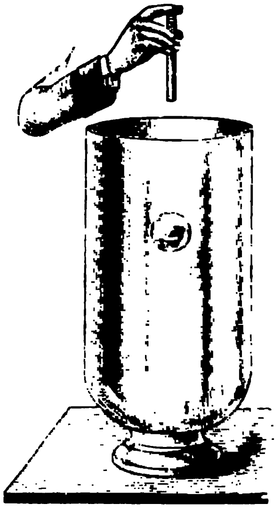

FIG. 61.

**Properties.**—Carbon dioxide is a colourless gas, having a feeble acid taste, and a faint and pleasantly pungent smell. It is incapable of supporting either combustion or respiration; a burning taper is instantly extinguished, and an animal speedily dies when introduced into this gas. Although carbon dioxide is not such a poisonous compound as the monoxide, it nevertheless does exert

oisonous effect upon the system, and death caused by
not merely due to the absence of oxygen. The pro-
alation of air containing only a very slightly increased
carbon dioxide, has a distinctly lowering effect upon
.

dioxide is a heavy gas, being about one and a half
ier than air. On this account it may readily be col-
displacement. By virtue of its great density it may be
m one vessel to another, much in the same way as an
quid : thus, if a large bell jar be filled with the gas by
nt, a beaker-full may be drawn up, as water from a
60). If the gas so drawn up be poured into a similar
pended from the arm of a balance, and counterpoised,
of the gas will be evident by the disturbance of the
of the system.

p bubble be allowed to fall into a large jar filled with
xide, it will be seen to float upon the surface of the
(Fig. 61). The power of carbon dioxide to extinguish
great, that a taper will not burn in air in which this gas
to the extent of 2.5 per cent., and in which the oxygen
to 18.5 per cent. For this reason a comparatively small
carbon dioxide, brought into the air surrounding a burn-
s capable of extinguishing the flame. This property has
valuable service in the construction of numerous con-
r extinguishing fire, such as the "extincteur." This is
sel containing carbon dioxide under pressure, the gas
n generated within the closed apparatus by the action
lphuric acid upon sodium carbonate. A stream of the
ted judiciously upon a moderate conflagration in a
eadily extinguishes the fire. This property may be
by inflaming a quantity of turpentine in a dish, and
on the flames a quantity of carbon dioxide contained
bell jar (Fig. 62), when it will instantly extinguish the
on.

h carbon dioxide is incapable of supporting combus-
ordinary sense, certain metals are capable of burn-
s gas. Thus, a fragment of potassium when heated
s, burns brightly, forming potassium carbonate with
tion of carbon—

$$2K_2 + 3CO_2 = 2K_2CO_3 + C.$$

When carbon dioxide is passed into a solution of calciu hydroxide (lime water) a turbidity at once results, owing to th precipitation of insoluble calcium carbonate, or chalk—

$$CaH_2O_2 + CO_2 = CaCO_3 + H_2O.$$

This reaction furnishes the readiest means for the detection o carbon dioxide. Thus, if the gas obtained by any of the modes o formation described, be passed into clear lime water, the formatio of this white precipitate of chalk, is proof that the gas is carbo dioxide. By this test it may readily be shown that carbon dioxid is a product of respiration, by merely causing the exhaled breat

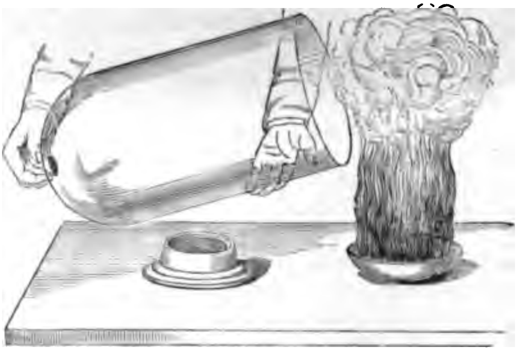

FIG. 62.

to bubble through a quantity of lime water, which will quickly b rendered turbid.

Carbon dioxide is moderately soluble in water. At the ordinar temperature, water dissolves about its own volume of this gas.

The coefficient of absorption at 0° is 1.7967, the solubility de creasing with rise of temperature in accordance with the inter polation formula—

$$c = 1.7967 - 0.07761t + 0.0016424t^2.$$

Carbon dioxide shows a slight departure from Henry's law (see page 123), when the pressures are greater than that of the atmosphere. Thus, when the pressure is doubled, the amount diss slightly more than doubled. The solubility of carbon in water, and its increased solubility under pressure, is ed in the ordinary aerated waters. Water under a pres-several atmospheres is saturated with the gas, and upon ase of this pressure by the withdrawal of the cork, the f gas, over and above that which the water can dissolve at nary pressure, escapes with the familiar effervescence. In r manner the natural aerated waters have thus become with carbon dioxide, under subterranean pressure, and ich waters come to the surface, the dissolved gas begins its escape.

olution of carbon dioxide in water is feebly acid, turning nus to a port-wine red colour, characteristically different e scarlet red given by stronger acids. This acid may be d as the true carbonic acid—

$$CO_2 + H_2O = H_2CO_3.$$

ently-made sample of aerated water is seen to effervesce iskly, and give off the dissolved gas more rapidly, than ns that have been long preserved. In process of time the d carbon dioxide gradually combines with the water, with ation of carbonic acid, an unstable compound which slowly oses into carbon dioxide and water, especially at a slight n of temperature. Many of the naturally occurring aerated such as Apollinaris, when opened, exhibit scarcely any cence, but give off carbon dioxide gradually. Such waters all probability been exposed to pressure for a great length and their dissolved carbon dioxide has almost entirely ed to form carbonic acid. When such a water is gently , a rapid stream of gas is evolved.

carbon dioxide is strongly heated, as by the passage of sparks, it is partially dissociated into carbon monoxide ygen. This decomposition is never complete; for when ount of these two gases in the mixture reaches a certain ion, they reunite to form carbon dioxide, and a point of ium is reached, when as many molecules are united as are ted in the same time.

**d Carbon Dioxide.**—Carbon dioxide is easily liquefied. it requires a pressure of 30.8 atmospheres ; at + 5°, 40.4 heres; while at + 15° a pressure of 52.1 atmospheres is l.

Faraday first liquefied this gas, by introducing into a strong bent glass tube a quantity of sulphuric acid, and a few lumps of ammonium carbonate, which were prevented from touching the acid by means of a plug of platinum foil. The tube was then hermetic[illegible] sealed, and the acid allowed gently to come in contact with [illegible] carbonate, which was at once decomposed with the formation [illegible] ammonium sulphate and carbon dioxide. By the internal pre[illegible]sure exerted by the evolved gas, aided by the application of co[illegible] to one end of the bent tube, the gas condensed to a colour[illegible] liquid.

Large quantities of this liquefied gas were obtained by Thilorie[illegible] by a precisely similar method, the experiment being performed i[illegible] strong wrought-iron vessels.

Liquid carbon dioxide is to-day manufactured on a large scale, by pumping the gas into steel cylinders by means of powerful compression pumps. The enormous volumes of carbon dioxide evolved in the process of brewing, and which until quite recently were allowed to escape into the atmosphere, are now utilised for this purpose. The gas, as it is evolved from the fermenting vats, is washed and purified, and pumped into steel bottles for the market. In this form the gas is largely employed by manufacturers of aerated waters.

Liquid carbon dioxide is a colourless and extremely mobile liquid, which floats upon water without mixing. It boils at −78°.2 under atmospheric pressure.

When heated, liquid carbon dioxide expands at a more rapid rate than a gas, its coefficient of expansion being greater than that of any known substance. Its rapid change of volume is seen by the following figures :—

| | | | | |
|---|---|---|---|---|
| 95 | volumes at | − 10° | become | |
| 100 | ,, | ,, | 0° | ,, |
| 106 | ,, | ,, | + 10° | ,, |
| 114 | ,, | ,, | + 20° | |

The critical temperature of carbon dioxide is 31.9°. If the liquid be heated to this point, it passes into the gaseous state without any change of volume. The line of demarcation, between the liquid and gas in the tube, gradually fades away, and the tube appears filled with gas. Above this temperature no additional pressure is able to liquefy the gas. On once more cooling the tube, when the ıl point is passed the liquid again appears, and the dividing etween it and the gas is once more sharply defined.

**ld Carbon Dioxide.**—When liquid carbon dioxide is allowed ape into the air, the absorption of heat due to its rapid evaon causes a portion of the liquid to solidify. This solid is conveniently collected, by allowing the jet of liquid to stream round metal box (Fig. 63), in which it is caused to revolve by made to impinge upon the curved tongue of metal. The box ished with hollow wooden handles, through which the gas its escape. Large quantities of the frozen carbon dioxide this way be collected in a few minutes.

d carbon dioxide is a soft, white, snow-like substance. When d to the air it quickly passes into gas, without going through ermediate state of liquidity.

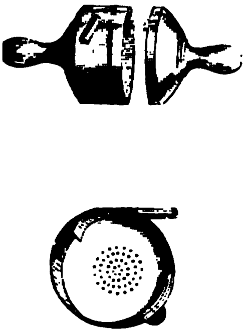

FIG. 63.

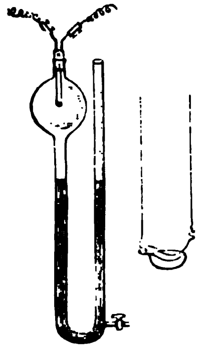

FIG. 64.

d carbon dioxide is readily soluble in ether, and this solution tutes one of the most convenient sources of cold. A large r of gases can readily be liquefied by being passed through immersed in this freezing mixture. When this ethereal n is rapidly evaporated, its temperature can be lowered to .

ırbonic acid snow," as this substance is sometimes termed, is n article of commerce, the compound being sent into the t in this form, to avoid the cost of the carriage of the sarily heavy steel bottles containing the liquid.

**nposition of *Carbon Dioxide*.**—When carbon burns in oxygen, the oxygen undergoes no change in volume in being transformed into carbon dioxide. The volume of carbon dioxide produced is the same as that of the oxygen which is required for its production. This may be shown by means of the apparatus, Fig. 64 The bulb of the U-tube is filled with oxygen, and the stopper which carries a small bone-ash crucible, upon which a fragmen of charcoal is placed, is lowered into position. The charcoal i ignited by means of a thin loop of platinum wire, as shown in th figure, which can be heated by an electric current. As the carbo burns, the heat causes a temporary expansion of the included gas but after the combustion is complete, and the apparatus ha cooled, the level of mercury will be found to be undisturbed Carbon dioxide, therefore, contains its own volume of oxygen From this experiment the composition of carbon dioxide by weigh can be deduced. One litre of carbon dioxide weighs 21.96 criths deducting from this the weight of 1 litre of oxygen, viz., 15.9 criths, we get 6 as a remainder. Six parts by weight of carbon therefore, combine with 15.96 parts by weight of oxygen to form 21.96 parts of carbon dioxide: expressing this proportion atomically, the proportion of carbon to oxygen is 12 to 31.92.

The gravimetric composition of carbon dioxide may be directl determined, by the combustion of a known weight of pure carbo in a stream of oxygen gas, and absorbing and weighing the carbo dioxide that is formed. This was done with great care an accuracy by Dumas and Stas, in the experiments by which the determined the atomic weight of carbon. Fig. 65 represents th apparatus employed for this purpose. A weighed quantity o diamond, contained in a small platinum boat, was introduced int a porcelain tube, which could be strongly heated in a furnace. Th oxygen for its combustion was contained in a glass bottle, from which it could be expelled by allowing water to enter through the funnel. As it was necessary that the oxygen should be absolutely free from any carbonic dioxide, the water used in the little gasholder contained potassium hydroxide in solution. The oxygen was then passed through the tubes A, B, C in order to deprive it of carbon dioxide and moisture, and lastly through a small desiccating tube, *d*, which was weighed before and after the experiment The pure dry oxygen then entered the strongly heated tube, and the carbon there burnt away to carbon dioxide, leaving a minute quantity of ash, which was carefully weighed at the conclusion of the experiment. A small layer of copper oxide was placed in the

tion indicated in the figure, in order to oxidise any
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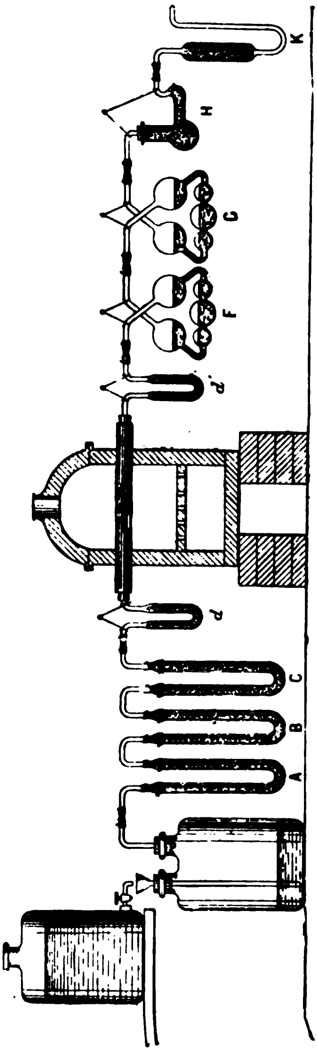

FIG. 65.

a number of experiments, Dumas and Stas found that 80 parts of oxygen by weight, combined with 29.99 parts of carbon.

From a knowledge of the density of carbon dioxide, and the volume of oxygen it contains, we know that the molecule of this gas contains two atoms ; therefore, by the simple equation—

$$80 : 31.92 :: 29.99 : 11.97,$$

11.97 parts of carbon combine with 31.92 parts of oxygen, and the number 11.97 is therefore the atomic weight of carbon as determined by these chemists.

**The Carbonates.**—Although carbonic acid, $H_2CO_3$, is a very unstable compound, the salts it forms are stable. Being a dibasic acid, it is capable of forming salts in which either one or both of the hydrogen atoms have been replaced by an equivalent of a metal ; thus in the case of sodium we have—

(1) Disodium carbonate (normal sodium carbonate) . $Na_2CO_3$.
(2) Hydrogen sodium carbonate (bicarbonate of soda) . $HNaCO_3$.

Similarly, with the divalent metal calcium, it is possible to form—

(1) Normal calcium carbonate . . . . . . . $CaCO_3$,

and—

(2) Hydrogen calcium carbonate (bicarbonate of lime) . $CaH_2(CO_3)_2$.

The formation of carbonates, by the action of carbon dioxide upon the hydroxides, may be illustrated by the following equations :—

$$2KHO + CO_2 = K_2CO_3 + H_2O.$$
$$CaH_2O_2 + CO_2 = CaCO_3 + H_2O.$$

The first of these changes is the one that takes place, when carbon dioxide is absorbed by the potassium hydroxide employed by Dumas and Stas in the course of their experiments, already described. The second equation represents the reaction which results, when carbon dioxide is passed into lime water, with the precipitation of chalk. In this latter case, if the gas be passed through the turbid solution for some time, the turbidity will gradually disappear, and the solution once more become clear. The normal calcium carbonate ($CaCO_3$) which is first formed, and which is insoluble, is converted into the soluble bicarbonate, $CaH_2(CO_3)_2$. If this solution be boiled, this unstable salt is decomposed with the evolution of carbon dioxide and water, and the reprecipitation of the normal calcium carbonate of lime—

$$CaH_2(CO_3)_2 = CaCO_3 + H_2O + CO_2.$$

The presence of this compound in natural waters is associated with the property known as the *hardness* of water (see Natural Waters, p. 197).

When one volume of dry carbon dioxide is mixed with two volumes of dry ammonia, the two gases unite, forming a compound known as ammonium carbamate—

$$CO_2 + 2NH_3 = CO_2,2NH_3 \text{ or } \left.\begin{matrix} HN_2 \\ NH_4O \end{matrix}\right\} CO,$$

which is the ammonium salt of the unknown carbamic acid, $\left.\begin{matrix} NH_2 \\ HO \end{matrix}\right\} CO$.

# CHAPTER X

## *COMPOUNDS OF CARBON WITH HYDROGEN*

THESE two elements unite together in various proportions, forming an enormous number of compounds, known generally under the name of the *hydrocarbons*. The reason for the existence of so great a number of compounds of these two elements, is to be found in the fact, that the atoms of carbon possess, in a very high degree, the property of uniting amongst themselves. This property of carbon gives rise to the formation of a number of groups or series of compounds, the members of which are related to each other, and to the simplest member of the series. Thus, the compound methane, $CH_4$, is the simplest member, or the "foundation-stone," of a series of hydrocarbons of which the following are the first four :—

| | | | |
|---|---|---|---|
| Methane . . . | $CH_4$ | Propane . . . | $C_3H_8$ |
| Ethane . . . . | $C_2H_6$ | Butane . . . | $C_4H_{10}$ |

It will at once be seen that each compound differs in composition from its predecessor, by an increment of $CH_2$, and that each may be expressed by the general formula, $C_nH_{2n+2}$.

In the following chapters the three hydrocarbons, methane, ethene, and acetylene, will be briefly studied. Each of these is a "foundation-stone," or starting-point, of a series similar to the one already mentioned ; thus

Methane, $CH_4$, first member of the $C_nH_{2n+2}$ series of hydrocarbons.
Ethene, $C_2H_4$, ,, ,, $C_nH_{2n}$ ,, ,,
Acetylene, $C_2H_2$, ,, ,, $C_nH_{2n-2}$ ,, ,,

### METHANE (*Marsh Gas—Fire-Damp*).

Formula, $CH_4$. Molecular weight = 16. Density = 8.

**Occurrence.**—Methane is found in the free state in large quantities in nature. It is one of the products of the decompositions which has resulted in the formation of the coal-measures. It is therefore found in enormous quantities in coal-mines, where it not only occurs in vast pent-up volumes, under great pressure, which escape with a rushing sound when the coal is being hewn; but it is also occluded within the pores of the coal. Methane is also evolved from petroleum springs.

The name marsh gas has been given to this compound, on account of its occurrence in marshy places, by the decomposition of vegetable matter. The bubbles of gas which rise to the surface when the mud at the bottom of a pond is gently disturbed, consist largely of marsh gas.

**Modes of Formation.**—(1.) When a mixture of sodium acetate and sodium hydroxide is strongly heated in a copper retort, sodium carbonate is produced and marsh gas is evolved—

$$CH_3 \cdot COONa + NaHO = Na_2CO_3 + CH_4.$$

The gas obtained by this reaction always contains more or less hydrogen.

(2.) Pure methane may be obtained by the decomposition of zinc methyl, by means of water—

$$Zn(CH_3)_2 + 2H_2O = ZnH_2O_2 + 2CH_4.$$

(3.) The most convenient method for preparing methane, is by the action of zinc-copper couple upon methyl iodide.* For this purpose the zinc-copper couple is placed in a small flask, and a mixture of equal volumes of methyl iodide and methyl alcohol is introduced by means of the stoppered funnel (Fig. 66). The gas is caused to pass through a tube filled with the zinc-copper couple, whereby it is deprived of any vapour of the volatile methyl iodide, and is collected over water in the pneumatic trough.

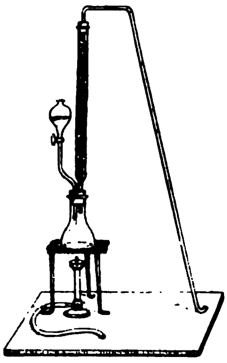

Fig. 66.

Marsh gas is formed during the process of the distillation of coal, and is therefore a large constituent of coal gas, the amount varying from 35 to 40 per cent.

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* "*Chemical Lecture Experiments*," No. 343.

**Properties.**—Methane is a colourless gas, having no taste or smell. It burns with a pale, feebly luminous flame. When mixed with air or oxygen and ignited, the mixture explodes with violence. The products of its combustion are water and carbon dioxide—

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

Methane is only about one-half as heavy as air, its specific gravity being 0.55 (air = 1). The *fire-damp* of coal-mines is nearly pure methane; its average composition being—

| | |
|---|---|
| Methane . . . . . . . | 96.0 |
| Carbon dioxide . . . . . | 0.5 |
| Nitrogen . . . . . . . | 3.5 |
| | 100.0 |

## ETHENE (*Ethylene—Olefiant Gas*).

Formula, $C_2H_4$. Molecular weight = 28. Density = 14.

**Modes of Formation.**—(1.) This compound is obtained, when ethyl iodide is acted upon by an alcoholic solution of potassium hydroxide—

$$C_2H_5I + KHO = KI + H_2O + C_2H_4.$$

(2.) It is also formed, when ethylene dibromide is brought in contact with zinc-copper couple, the ethylene dibromide being diluted with its own volume of alcohol—

$$C_2H_4Br_2 + Zn = ZnBr_2 + C_2H_4.$$

(3.) The method usually employed for preparing ethylene in quantity, consists in abstracting the elements of water from alcohol, by means of strong dehydrating agents, such as phosphorus pentoxide, or sulphuric acid—

$$C_2H_6O - H_2O = C_2H_4.$$

The mixture of alcohol and sulphuric acid is heated in a flask to about 165°; and the ethylene, after being washed by bubbling through water, may be collected at the pneumatic trough.*

**Properties.**—Ethylene is a colourless gas, having a somewhat pleasant ethereal smell; it burns with a highly luminous flame, forming carbon dioxide and water, one volume of the gas requiring three volumes of oxygen for its complete combustion—

---

* "Chemical Lecture Experiments," Nos. 438 to 441.

$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O.$$

If mixed with oxygen in this proportion and inflamed, the mixture explodes with great violence.

When mixed with twice its volume of chlorine and ignited, the mixture burns rapidly with a lurid flame, with the formation of hydrochloric acid and deposition of carbon—

$$C_2H_4 + 2Cl_2 = 4HCl + 2C.$$

Ethylene is reduced to the liquid state, at a temperature of 0°, by a pressure of 41 atmospheres; the critical temperature of the gas is + 10.1°, at which point a pressure of 51 atmospheres is required to liquefy it. Liquefied ethylene boils at − 103°, and by increasing its rate of evaporation, temperatures as low as − 140° can readily be obtained; this substance, therefore, furnishes an extremely useful refrigerating agent when very low temperatures are required, as, for example, in the liquefaction of oxygen, nitrogen, and other gases having low critical points. Ethylene (together with higher members of the same series) constitutes the chief illuminating constituent of ordinary coal gas, of which it forms from 4 to 10 per cent.

### ETHINE (*Acetylene*).

Formula, $C_2H_2$. Molecular weight = 26. Density = 13.

**Modes of Formation.**—(1.) Acetylene is capable of being synthetically formed by the direct union of its elements. For this purpose a stream of hydrogen is passed through a three-way globe, in which an electric arc is burning between two carbon rods, arranged as seen in Fig. 67 (a quantity of sand being placed in the globe, to prevent fracture from falling fragments of red-hot carbon). Under these circumstances, a small quantity of the carbon and hydrogen unite to form acetylene, which is swept out of the globe by the current of hydrogen.

(2.) Acetylene is more conveniently prepared by the action of alcoholic potash upon *ethylene dibromide*. Alcoholic potash is heated in a flask, and ethylene dibromide dropped upon it from a stoppered funnel, when the following reaction takes place[*]—

$$C_2H_4Br_2 + 2KHO = 2KBr + 2H_2O + C_2H_2.$$

(3.) Acetylene may also be obtained by the action of water upon barium carbide;[†] thus—

$$BaC_2 + 2H_2O = BaH_2O_2 + 2C_2H_2.$$

(4.) Acetylene is formed when marsh gas, or coal gas, is burned with an insufficient supply of air for complete combustion; thus, when a Bunsen lamp becomes accidentally ignited at the base of the chimney, the peculiar and unpleasant smell that is perceived is due to the formation of acetylene.

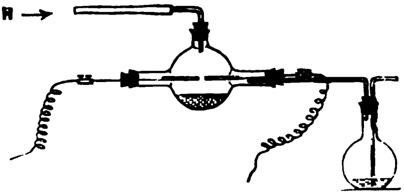


FIG. 67.

Acetylene is present in small quantities in ordinary coal gas.

**Properties.**—Acetylene is a colourless gas having an extremely offensive smell, which rapidly induces headache; when inhaled in an undiluted state it is poisonous. The gas burns with a highly luminous and smoky flame. It is more soluble in water than either ethylene or marsh gas; water at the ordinary temperature dissolving about its own volume of this gas. At a temperature of + 10°, and under a pressure of 63 atmospheres, acetylene condenses to a colourless liquid.

When acetylene is passed into an ammoniacal solution of cuprous chloride, a deep-red coloured compound is produced, known as cuprous acetylide—

$$Cu_2Cl_2,2NH_3 + H_2O + C_2H_2 = 2NH_4Cl + C_2H_2Cu_2O.$$

---

[*] "Chemical Lecture Experiments," No. 448.

[†] Barium carbide may be obtained by heating a mixture of two parts of barium carbonate, four of carbon (powdered gas carbon), and ten of powdered magnesium, in a copper flask.

his reaction furnishes not only a ready and delicate test for the resence of this gas, but also a means of removing acetylene from admixture with other gases, and obtaining it in a form of combination from which it can easily be disengaged again in a state of purity.

Large quantities of this compound may readily be obtained, by aspirating the products of the imperfect combustion of coal gas, through ammoniacal cuprous chloride. For this purpose, a flame of air burning in an atmosphere of coal gas (see Combustion, page 268) is arranged as seen in Fig. 68, and the products of combustion are drawn through the copper solution contained in the cylinder, by means of a suitable aspirator. The cuprous acetylide rapidly forms as a red precipitate, which can be separated from the solution by filtration.

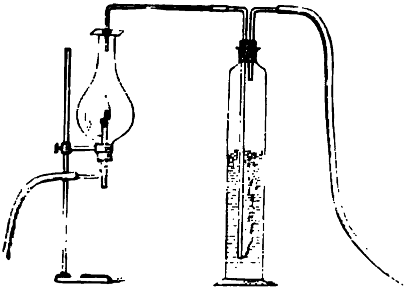


FIG. 68.

From this substance, pure acetylene is readily obtained by the addition to it of hydrochloric acid—

$$C_2H_2Cu_2O + 2HCl = Cu_2Cl_2 + H_2O + C_2H_2.$$

**Coal Gas.**—When coal is distilled, the volatile products obtained are: (1) coal tar; (2) an aqueous liquid containing ammonia and other products, and known as *ammoniacal liquor*; (3) *coal gas*.

Coal gas, after being subjected to ordinary purification, is a mixture of gases which may be divided into three classes, namely: *illuminants*, *diluents*, and *impurities*. The most important of these substances are—

*Illuminants.*
Ethylene, $C_2H_4$; propylene, $C_3H_6$; butylene, $C_4H_8$ . . . . . . $(C_nH_{2n})$
Acetylene, $C_2H_2$; allylene, $C_3H_4$ . $(C_nH_{2n-2})$
Benzene, $C_6H_6$ . . . . . . $(C_nH_{2n-6})$
About 6.5 per cent.

*Diluents.*—Hydrogen, marsh gas, carbon monoxide . About 90 per cent.

*Impurities.*—Nitrogen, carbon dioxide, sulphuretted hydrogen . . . . . . . About 3.5 per cent.

The composition of the gas is largely determined by the nature of the coal employed, as may be seen from the following analyses of gas from bituminous and from cannel coal:—

| | *From Bituminous Coal.* | | *From Cannel Coal,* | |
|---|---|---|---|---|
| | London (Frankland). | | London (Frankland). | Manchester (Bunsen and Roscoe). |
| Hydrogen . . . . | 50.05 | 51.24 | 35.94 | 45.58 |
| Marsh gas . . . . | 32.87 | 35.28 | 41.99 | 34.90 |
| Carbon monoxide . . | 12.89 | 7.40 | 10.07 | 6.64 |
| Illuminants . . . . | 3.87 | 3.56 | 10.81 | 6.46 |
| Nitrogen . . . . | ... | 2.24 | ... | 2.46 |
| Carbon dioxide . . . | 0.30 | 0.28 | 1.19 | 3.67 |
| Sulphuretted hydrogen . | ... | ... | ... | 0.29 |
| | 100.00 | 100.00 | 100.00 | 100.00 |

# CHAPTER XI

## *COMBUSTION*

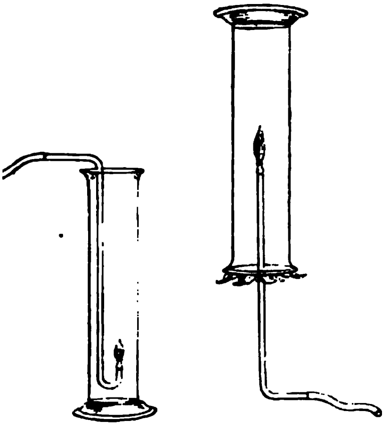
WHEN chemical action is accompanied by light and heat, the phenomenon is called *combustion*. All exhibitions of light and heat are not necessarily instances of combustion; thus, when an electric current is passed through a spiral of platinum wire, or through a carbon thread in a vacuous bulb (as in the familiar "glow" lamps), these substances become hot, and emit a bright light. Neither the platinum nor the carbon, however, is undergoing any chemical change, and therefore the phenomenon is not one of combustion. The materials are simply being heated to a state of incandescence by external causes, and as soon as these cease to operate, the glowing substances return to their original condition unchanged.

Combustion may be defined as *the chemical union of two substances, taking place with sufficient energy to develop light and heat.* When the amount of light and heat are feeble, the combustion is described as *slow* or *incipient;* while, on the other hand, when they are considerable, the combustion is said to be *rapid* or *active.* The true nature of combustion was not understood until after the discovery of oxygen in 1775. From about the year 1650 until after that important discovery, the phlogistic theory was universally adopted. According to this view, a combustible body was one which contained, as one of its constituents, a substance or *principle* to which the name *phlogiston* was applied. Easily combustible substances were considered to be rich in phlogiston, while those that were less inflammable were held to contain but little of this ingredient. The act of combustion, was regarded as the escape of this principle from the burning substance. Thus, when a metal was burnt in the air, it was considered to be giving off its phlogiston, and the material that was left after the combustion (which we now know to be the oxide of the metal) was regarded as the other constituent *of the metal,* and was called the *calx.* The metal, therefore, was supposed to be a compound of a calx with phlogiston. By heating a calx along with some substance rich in phlogiston, the former again combined with this principle and the metal was once more produced. Thus, when the calx of lead was heated with charcoal (a substance pre-eminently rich in phlogiston), the charcoal supplied the calx with the necessary amount of phlogiston, to produce the compound of calx of lead and phlogiston, which was metallic lead. This theory of combustion, after sustaining many severe shocks (from such experiments as those of Boyle and others, who showed that the calx of a metal was *heavier* than the metal used in its formation), received its death-blow on the discovery of the compound nature of water, and that this substance was produced by the combustion of hydrogen in oxygen.

In all processes of combustion, it is customary to regard one of substances taking part in the chemical change as the *combustible*, and the other as the *supporter of combustion*. Usually that substance which surrounds or envelops the other, is called the *supporter of combustion*. Thus, when a jet of burning hydrogen is introduced into a jar of chlorine, or when a fragment of charcoal burns in oxygen, the chlorine and the oxygen are spoken of as the *supporters of combustion*, while the hydrogen and carbon are termed the *combustibles*.

In all the more familiar processes of combustion, the atmosphere itself is the enveloping medium, and the air is therefore, *par excellence*, the supporter of combustion ; and in ordinary language the terms *combustible* and *incombustible* are applied to denote substances which burn, or do not burn, in the air. By a similar process of limitation, it has become customary to speak of other gases as supporters or non-supporters of combustion, if they behave towards ordinary combustibles as air does. Thus we say of hydrogen, or marsh gas, or coal gas, that they are combustible, but do not support combustion ; and of oxygen, or chlorine, or nitrous oxide, that they do not burn, but will support combustion ; and, lastly, of such gases as ammonia, or carbon dioxide, or sulphur dioxide, that they neither burn nor support combustion.

This distinction, however, is a purely conventional one, and has little or no scientific significance ; for, by a slight modification of the conditions, either hydrogen, marsh gas, or coal gas may become supporters of combustion, and oxygen, chlorine, or nitrous oxide the combustible substances. Thus, when a jet of hydrogen burns in oxygen, we say that the hydrogen is the combustible, and the n the supporter of combustion (Fig. 69, A); but if a jet of n be thrust up into a jar of hydrogen (Fig. 69, B), it ignites as it s the burning hydrogen, and continues to burn in the hydrogen. means of the apparatus shown in Fig. 70, this may be still strikingly shown.* A stream of hydrogen is passed into the chimney by the tube H, and the issuing gas inflamed as it es at the top. Oxygen is admitted through the tube O, and t of gas ignited by pushing the long tube up into the burning gen at the top, and then drawing it down to the position



A FIG. 69. B

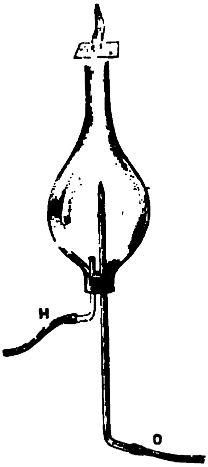


FIG. 70.

wn in the figure, where the jet of oxygen continues to burn in atmosphere of hydrogen.

y means of the same apparatus, oxygen, or chlorine, or nitrous le, may be caused to burn in either hydrogen, marsh gas, or l gas. Ammonia, which, as already mentioned, is usually cribed as being neither combustible nor a supporter of comtion, when surrounded by an atmosphere of oxygen is readily ammable, and will as readily support the combustion of oxygen. The atmosphere itself becomes the combustible body when the al conditions of combustion are reversed. Thus, if a stream of coal gas be passed through a similar lamp glass, through the cork of which a short straight glass tube passes (Fig. 71), air will be drawn up through this tube, and may be inflamed by passing up a lighted taper. The jet of air will then continue to burn as a non-luminous flame. The air is here the combustible, and the coal gas the supporter of combustion. If the excess of coal gas be inflamed as it escapes from the top, the opposite conditions will be fulfilled, the air being the supporter of combustion, and the coal gas the combustible.

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* "*Chemical Lecture Experiments*," No. 352.

This interchangeableness of the terms combustible and supporter of combustion, applies also to substances that are liquid or even solid, at the ordinary temperature. If a small quantity of some inflammable liquid, as ether, carbon disulphide, turpentine, &c., be boiled in a flask, and the issuing vapour inflamed, a jet of oxygen gas when lowered into the flask will ignite as it passes the flame, and continue to burn in the vapour of the liquid. In the same way, sulphur, which is a combustible solid, and whose vapour is inflammable in the air, is capable in the state of vapour of supporting the combustion of oxygen. Since combustion is the result of energetic chemical union, and since also it is a mere condition of experiment which of the two acting substances shall function as the environment of the other, it will be seen that the terms combustible and supporter of combustion, as applied to a chemical substance, do not express any definite or characteristic property of that body.

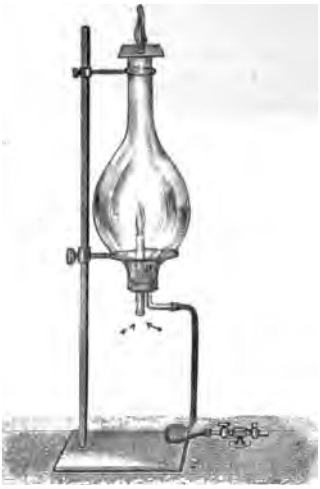

Fig. 71.

It was demonstrated by Boyle, that when a metal is burnt in the air, the calx (or oxide) that is obtained, weighs *more* than the metal employed, instead of less, as the phlogistic theory seemed to demand. This fact, which the upholders of phlogiston found it so difficult to reconcile, is seen to be a necessary consequence of considered from the modern point of view. In all combustion, the weight of the products of the action he total weight of each of the two substances taking hemical combination. When, for example, the metal burns in the air, the weight of the product of the com- ual to the weight of the metal, *plus* the weight of a int of oxygen with which it united in the act of burn- ain in weight during combustion may be demonstrated of ways. Thus, if a small heap of finely divided iron, the reduction of the oxide, be counterpoised upon the alance, and then iron will be seen d as it burns the l show that the mass is increasing In this case the of the combustion substance, namely, hich remains upon the balance ; but sult follows when of the action is Thus, for instance, ment of sulphur is ugh it disappears it, like the iron, ith oxygen to form his oxide, however, escapes into the If the sulphur be ch a manner that dioxide is collected and weighed, it also will be found r than the original sulphur. In the process of burn- me of sulphur unites with about 1 gramme of oxygen, oduct therefore weighs 2 grammes. By causing an ndle to burn in the apparatus shown in Fig. 72, where products of its combustion are arrested, the increase may easily be seen. The candle being essentially a of carbon and hydrogen, the products of its burning bon dioxide and water, both of which will be absorbed um hydroxide in the upper part of the tube. Conse-

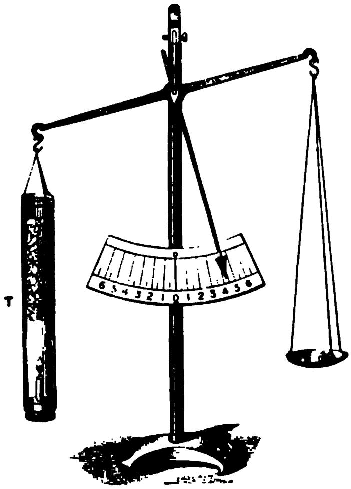

FIG. 72.

quently, as the candle burns away, the arrangement gradually gains in weight; the increase being the weight of the atmospheric oxygen which has combined with the carbon and the hydrogen, form the compounds carbon dioxide and water.

**Heat of Combustion.**—During the process of combustion, certain amount of heat is evolved, and a certain temperature attained—two results which are quite distinct. The *temperature* measured by thermometers, or pyrometers, while the *amount* *heat* is measured in terms of the *calorie*, or heat unit.*

The amount of heat produced by the combustion of any substance, is the same, whether it burns rapidly or slowly, provided always that the same final products are formed in each case. Thus, when 1 gramme of phosphorus burns in the air to form phosphorus pentoxide, it evolves 5747 calories; and when the same weight of phosphorus is burnt in oxygen, although the combustion is much more rapid and energetic, and the *temperature* consequently rises higher, the *amount of heat* evolved is precisely the same.

Again, when iron is heated in oxygen it burns with great brilliancy, and with evolution of much heat; if, however, the same weight of iron be allowed slowly to combine with oxygen, even without any manifestation of combustion, but simply by the process of spontaneous oxidation, or *rusting*, it is found that the *amount of heat* produced, in forming the same oxide, is absolutely the same.

So far, therefore, as the quantity of heat produced is concerned, there is no difference between *active* combustion and *slow* combustion, or (confining ourselves to the case of combinations with oxygen) between active combustion and the ordinary process of spontaneous oxidation at ordinary temperatures. In the latter case the heat is given out slowly; so slowly that it is conveyed away by conduction and radiation as fast as it is produced, and consequently the *temperature* of the material undergoes no perceptible change. In the case of active combustion, the action is crowded into a few minutes or seconds, and, as all the heat developed is evolved in this short space of time, the temperature of the substances rapidly rises to the point at which light is emitted.

That heat is developed during the process of spontaneous oxidation is readily shown. Thus, if a small heap of fragments of osphorus be exposed to the air, it will be evident from the mation of fumes of oxide, that it is undergoing oxidation. As e action proceeds, and as the heat produced by the oxidation is veloped more rapidly than it is radiated away (especially from e interior portions of the heap), it will be seen that the phosorus quickly begins to melt, and finally the temperature will e to the point at which *active* combustion begins, when the mass ll burst into flame.

---

* The major calorie sometimes used is equal to 1000 calories. See Thermochemistry, Part I. chap. xv.

It has been shown, that many destructive fires have arisen from asses of combustible material, such as heaps of oily cotton waste, dergoing this process of spontaneous oxidation, until the heat veloped within the mass has risen sufficiently high to inflame e material. To the operation of the same causes, is to be ferred the spontaneous firing of hay-stacks which have been ilt with damp hay; and also the spontaneous inflammation of al in the holds of ships.

As the temperature produced by combustion is augmented by creasing the rapidity with which the chemical action takes place, will be at once obvious why substances which burn in the air, urn with increased brilliancy and with higher temperature in pure xygen. In the air, every molecule of oxygen is surrounded by ur molecules of nitrogen, therefore for every one molecule of xygen that comes in contact with the burning substance, four olecules of this inert element strike it; and by so doing they not nly prevent the contact of so much oxygen in a given interval of ime, but they themselves have their temperature raised at the xpense of the heat of the burning material. The number of xygen molecules coming in contact with a substance burning in the air, in a given time, may be increased by artificially setting the air in rapid motion: hence the increased rapidity of combustion (and consequent rise of temperature) that is effected by the use of bellows, or by increasing the draught by means of chimneys and dampers.

The augmentation of temperature obtained by the substitution of pure oxygen for air, is well illustrated in the case of burning hydrogen. The temperature of the flame of hydrogen burning in oxygen, known as the oxy-hydrogen flame, is extremely high, and when allowed to impinge upon a fragment of lime, it quickly raises the temperature of that substance to an intense white heat, when it emits a powerful light—the so-called *oxy-hydrogen lime light.*

The following results obtained by Bunsen, show the temperatures reached by the combustion of hydrogen, and of carbon monoxide, in air and in oxygen :—

| | |
|---|---|
| The flame of hydrogen burning in air . . . | 2024° |
| „ „ „ oxygen . . | 2844° |
| „ carbon monoxide burning in air . | 1997° |
| „ „ „ oxygen | 3003° |

It will be seen that whereas the flame of hydrogen in air is hotter than that of carbon monoxide in air, when these gases burn in oxygen the temperature of the carbon monoxide flame is higher than that of hydrogen. This is due to the partial dissociation of the water, which results from the combustion of the latter. It has been shown that when a mixture of hydrogen and oxygen, in the proportion to form water, is ignited, the temperature produced by the union of a portion of the mixture, rises above the point at which water dissociates; and consequently for a certain small interval of time, a condition of equilibrium obtains, during which as many molecules of water are dissociated as are formed: during this state the temperature falls, when rapid combustion once more proceeds. It will be seen, therefore, that the limits to the temperature which can be reached by combustion, are influenced by the point at which the products of combustion undergo dissociation.

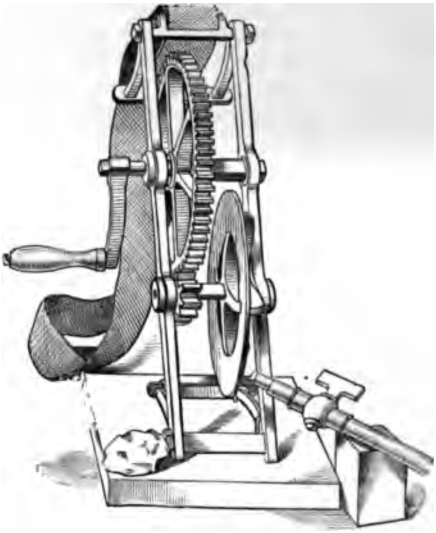

FIG. 73.

**Ignition Point.**—The temperature to which a substance must be raised, in order that combustion may take place, is called its *ignition point*. Every combustible substance has its own ignition temperature. If this point be below the ordinary temperature, the substance will obviously take fire when brought into the air, without the application of heat: such substances are said to be *spontaneously inflammable*, and must necessarily be preserved out of contact with air.

Passing from cases of spontaneous inflammability, we find a very wide range existing between the igniting points of different substances. Thus, a jet of gaseous phosphoretted hydrogen may be ignited, by causing it to impinge upon a test-tube containing boiling water: carbon disulphide vapour is inflamed by a glass rod heated to 120°, while the diamond requires to be raised nearly to a white heat before combustion begins.

The difference between the temperatures of ignition of hydrogen, and marsh gas, may be well seen by means of the old *steel mill* of the miner (Fig. 73). By causing the steel disk to revolve at a high speed, while a fragment of flint is lightly pressed against its edge, a shower of sparks is thrown out; and on directing a jet of hydrogen upon these sparks, the gas is instantly ignited, while they may be projected into a stream of marsh-gas without causing its inflammation. The same fact is also made strikingly apparent by depressing a piece of fine wire gauze upon flames of marsh gas (or coal gas), and hydrogen. In the former case, the flame will not pass through the gauze, although it may be shown that marsh gas is making its way through, by applying a lighted taper immediately above the wire. If the gauze be held over the issuing jet of gas, the latter may be ignited by a taper upon the upper side of the gauze, but the combustion will not be communicated to the inflammable gas beneath (Fig. 74). The gauze conducts the heat away from the flame so rapidly, that the temperature of the metal does not rise to the ignition point of the marsh gas on the other side, and therefore the combustion cannot be propagated through the gauze.

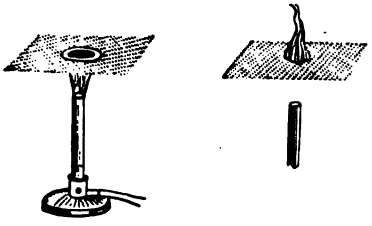

FIG. 74.

In the case of hydrogen, however, it will be found that the instant the gas upon the upper side of the gauze is inflamed, the flame passes through, and ignites the hydrogen beneath.[*]

It is upon this principle that the safety of the "Davy lamp" depends. This consists of an ordinary oil lamp, the flame of which is surrounded by a cylinder of wire gauze (usually made double at the top), through which air to supply the flame freely passes in, and the products of combustion pass out. When such a lamp is taken into an atmosphere in which marsh gas is present, this gas, entering through the gauze, becomes ignited within the chimney, producing a very characteristic effect upon the lamp flame. According to the amount of marsh gas present, the flame is seen to become more and more extended, at the same time becoming less luminous, until the whole interior of the gauze cylinder is filled with the burning gas, emitting a faint bluish light, known among the miners as the *corpse-light*. The burning marsh gas is unable to communicate its combustion to the inflammable mixture outside, for the same reason that the flame, in the experiment already referred to, was unable to pass through the wire gauze. If from any cause, the flame should heat any spot of the gauze chimney to a temperature above the ignition point of marsh gas, the outside combustible mixture will become ignited. It has been shown, that by exposing the lamp to a strong air draught, the flame may be so driven against the gauze as to unduly heat the metal. It has also been proved, that the same result frequently follows from the explosive wave that is produced in a mine, when, from some accidental cause, the operation of blasting (or *shot-firing*) results, not in the splitting of the rock, but in merely blowing out the "tamping." The violent concussion to the air, which follows such a *blown-out shot*, has been known to blow the flames of the Davy lamps, even in remote parts of the workings, bodily through the gauze; and if such lamps are burning at the time in an inflammable mixture, it would thereby be fired.

By the behaviour of the flame of a Davy lamp, when placed into an atmosphere containing marsh gas, it is possible to estimate, with a rough degree of accuracy, the percentage amount of that gas which is present. For this purpose the flame is turned down as low as possible, and the height to which the burning marsh gas extends (the so-called *fire-damp cap*) is measured against a scale graduated in tenths of inches. Fig. 75 (two-thirds the actual size) shows the "caps" obtained by the presence of 4, 5, and 6 per cent. of marsh gas.[†]

When the ignition point of a substance is lower than the temperature produced by its combustion, such a substance, when

---

[*] Recent experiments of Victor Meyer (*Berichte*, No. 16, 1893), upon the ignition temperature of explosive gaseous mixtures, give the following results:—

| | |
|---|---|
| A mixture of oxygen and hydrogen (electrolytic gas) explodes at | 612° |
| Explosive mixture of oxygen and marsh gas . . . . . | 656° |
| ,, ,, ,, coal gas . . . . . | 647° |

[†] In a recent development of this method of testing, a small hydrogen flame is substituted for the oil lamp flame, whereby it is possible to detect the presence of 0.25 per cent. of marsh gas (Clowes).

d, will continue to burn without further application of ex- l heat, the inflammation being propagated from particle to le by the heat developed by their own combustion. All the ary processes of combustion are actions of this order, and g to the class of chemical reactions known as *exothermic*, s to say, reactions which are accompanied by an evolution it (page 147).

on the other hand, the ignition point be higher than the heat iced by chemical union, combustion cannot proceed without ntinuous application of external heat. The igniting point of

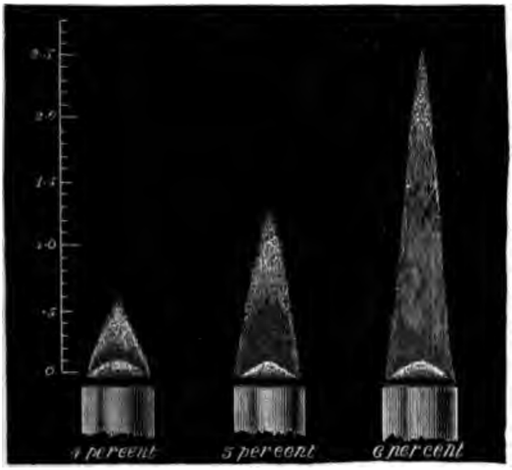

FIG. 75.

gen in oxygen, for example, is higher than the temperature iced by the union of these elements; therefore, although the gen may be ignited by the heat of the electric spark, it is le to communicate its combustion to contiguous particles, and nflammation does not spread. If the ignition point of nitro- in oxygen had been *lower* instead of *higher* than the heat of hemical union of these elements, the first flash of lightning that arged into the air would have initiated a conflagration, which d have extended through the whole atmosphere, and resulted le removal of the oxygen, and its replacement by oxides of gen.

The production of acetylene by the combination of carbon with hydrogen under the influence of high temperature; and the formation of cyanogen, and carbon disulphide, by the union of the same element with nitrogen and with sulphur respectively, are illustrations of the same class of action: phenomena of this order being known as *endothermic* reactions, that is, reactions that are attended with an absorption of heat (page 147).

**Flame.**—When both the substances taking part in combustion are gases or vapours, the sphere of the chemical action assumes the character of flame; while, on the other hand, if one of the materials is a solid which is not volatile at the temperature of its combustion, no flame accompanies its burning. Such solids as sulphur, phosphorus, camphor, wax, &c., during combustion in air, undergo vaporisation, and consequently burn with the formation of flame; while such substances as iron, copper, carbon,* &c., which do not pass into vapour at the temperature produced by their combustion in oxygen, burn in this gas without giving rise to a flame.

Flames differ very widely in their general appearance, and in the majority of cases are distinctly characteristic: thus, hydrogen burns in air with a flame that is almost absolutely colourless, and is scarcely visible in bright daylight; sulphur burning in air produces a pale blue flame; ammonia in oxygen a flame having a yellow-ochre colour; carbon monoxide a rich blue flame, while cyanogen burns with a flame having the delicate colour of the peach blossom. Other flames are characterised by their luminosity. Thus, phosphorus burning in oxygen emits a dazzling yellow light, that is almost blinding to the eyes; magnesium burns in the air with an intense bluish-white light; the flame produced by the combustion of the vapour of nickel carbonyl in air emits a bright white light; and the flames that are produced by most hydrocarbons during their combustion, give a characteristic yellowish-white light.

**The General Structure of Flame.**—The simplest form of flame, is one that is obtained by the combustion of a substance which itself undergoes no decomposition, and in which the product of combustion is arrived at in a single stage. Such flames, for example, as that of hydrogen burning in chlorine or in air; or of carbon monoxide burning in air. In the case of hydrogen burning in air, the materials taking part in the process being elementary bodies, no complications arising from decomposition are possible; and although carbon monoxide is a compound, it unites with oxygen without itself undergoing any decomposition, and passes directly into carbon dioxide. Such flames as these, when burning from the end of a tube, consist of a single hollow conical sheath of actively burning gas. Fig. 76 represents a flame of burning hydrogen: the darker region *d* is the hollow space within the flame, consisting of unburnt hydrogen; while the flame proper, the actual burning portion, is the sheath *b*, which appears practically uniform throughout. That the flame-cone is hollow may be proved by a variety of experiments. Thus, if a sheet of white paper be quickly depressed into a flame, a charred impression of the section of the cone will be obtained, as shown in Fig. 77, from which it will be seen that no combustion is taking place within the cone. In the same way, an ordinary lucifer match may be suspended within the flame, where it will remain without ignition so long as the burning walls of the flame do not touch it. The shape of a flame is due to the fact, that as the gas issues, the layer nearest to the walls of the tube burn round the orifice of the tube as a ring, consequently the next layer has to reach up above this ring before it can meet with air for its combustion, and each successive layer has to pass up higher and higher in order to find its supply of air, and in this way the burning area is built up into the form of a cone. To show that the hollow space consists of unburnt gas, it is only necessary to insert a tube into the interior of the flame in such a way as to

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* Under certain conditions, the combustion of carbon in oxygen is accompanied by flame; but it has been shown that at the temperature at which this occurs, carbon monoxide is being formed.

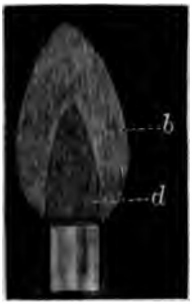

FIG. 76.

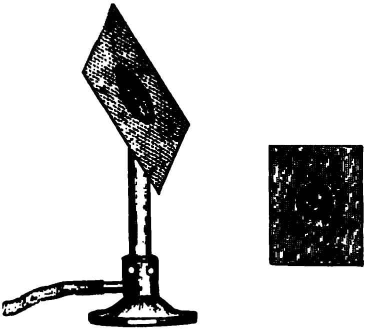

FIG. 77.

draw off a portion of the gas, when it will be found that the withdrawn will burn.

Passing from this simplest type, to substances that u decomposition during combustion, or which yield the final p of oxidation by successive stages, it is found that the flame give rise to are less simple in structure.

As illustrations of various degrees of complexity, the fol examples may be mentioned :—

(1.) Ammonia burning in oxygen. This flame (Fig. 78) characteristic, and on inspection it is at once obvious that i less simple structure than the hydrogen flame. In this c inner hollow portion *d* is surrounded by a double flame-co inner cone *a* having a yellow-ochre colo the outer portion *b* possessing a much colour, and tending to green. Duri combustion of ammonia, the compound goes decomposition into nitrogen and gen. This decomposition, which begins hollow region *d*, takes place mainly in th cone *a*, and the hydrogen which escape bustion in this region, passes to the o and there burns, forming the outer cone. bably there is also a partial combustion nitrogen.

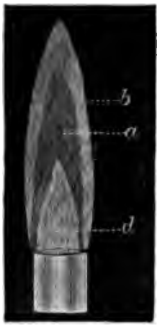

FIG. 78.

(2.) Carbon disulphide burning in air. flame, like the ammonia flame, consist double flame-cone, consisting of an inne coloured cone, surrounded by an outer having a deeper blue colour. During combustion, carbon phide, like ammonia, is decomposed, but in this case not o *both* of the constituents readily combustible, but the carbon into its final state of oxidation in two stages, forming first c monoxide and afterwards carbon dioxide.

(3.) Hydrocarbons burning in air. The flames produced combustion of these compounds, include those which are com employed for illuminating purposes, such as candle, gas, a flames, and in all essential points of construction they are cally identical. This may be seen to be the case by a comp of the flames of a candle and of coal gas (Figs. 79 and 80 these flames, as in the former cases, there is the dark hollow *d*, consisting of heated unburnt gas (in the candle flame th ated by the vaporisation of the materials of the candle, the melted condition are drawn up the wick by capillary Above this there is a region, *a*, which, in comparison : rest of the flame, appears almost opaque, and which bright yellow light. This luminous area constitutes relae largest part of the flame, and in flames that are used for ing purposes, it is intentionally made as large as possible .s of various devices. At the base of the flame, there is region, *c*, which appears bright blue in colour, and is non-

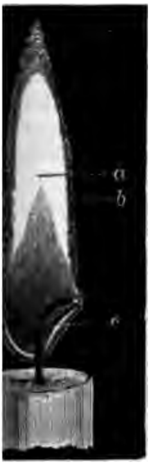

FIG. 79.

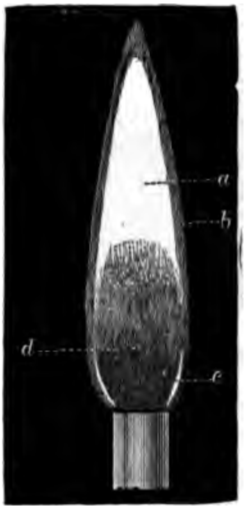

FIG. 80.

s; and surrounding the entire flame there will be seen a ıminous mantle, *b*.

lame proper, therefore, consists of three distinct parts, (1) the blue region *c*, at the base; (2) the faintly luminous ; and (3) the yellow, brightly luminous region *a*. These rts constitute the flame-cone, the actual area of combustion, ıvelops the dark region *d*; this, as already stated, consists nt gas, and therefore is not, strictly speaking, a part of the

supply of gas to a flame, burning as represented in Fig. 80, be diminished, or if air be slowly admitted to the interior, the flame will shrink down, and the luminous area become less and less, until it finally disappears altogether. The flame-cone will then be found to consist of two parts, resembling in structure the double cone of the ammonia flame, Fig. 78. The blue region *c*, Fig. 80, which is only fragmentary in the flame as there represented, will have become continuous, and now constitutes the inner cone; while the mantle *b* forms the outer cone, the flame presenting the appearance seen in Fig. 81. The region *d*, as before, consists of unburnt gas.

It has been shown, in the case of coal gas flames burning in this manner, that in the inner cone *c*, the changes going on result mainly in the formation of carbon monoxide and water, together with small quantities of carbon dioxide and hydrogen; and that in the outer cone, or mantle, the carbon monoxide and hydrogen are burning to carbon dioxide and water. In the inner cone, therefore, the carbon is burnt to its first stage of oxidation, and a portion of the hydrogen is oxidised to water; in the outer cone, the second stage of oxidation of the carbon takes place by the combustion of the carbon monoxide to carbon dioxide, and the hydrogen which escapes combustion in the inner cone is also burnt.

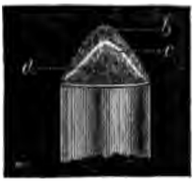

FIG. 81.

It has been known since the time of Dalton, that when certain hydrocarbons are burnt with an insufficient amount of oxygen for the complete oxidation of both the hydrogen and carbon, carbon monoxide, water, and hydrogen are produced. This result is probably due to a secondary reaction; the first stage being the combustion of hydrogen to form water, which at the high temperature is then decomposed, either by the carbon, or the hydrocarbons, according to the following equations—

$$CH_4 + O_2 = 2H_2O + C = CO + H_2 + H_2O.$$
$$C_2H_4 + O_2 = 2H_2O + 2C = 2CO + 2H_2.$$

The various parts of an ordinary gas or candle flame, therefore, are due to the different chemical reactions that are taking place in these areas; these changes are not of such a nature that they can in all cases be perfectly traced, neither is one set of reactions exclusively confined to each area, but rather is it the case that certain chemical actions predominate in each particular part of the flame.

In the blue region *c*, Figs. 79 and 80, the main reactions going forward are those already indicated, by which carbon monoxide, water, and hydrogen are produced. In the faintly luminous mantle *b*, carbon monoxide and hydrogen are burning, together with small quantities of hydrocarbons which may have escaped combustion and decomposition in the luminous region. The non-luminous character of this mantle, is due to the cooling effect of the air which is drawn into the flame, and which even extinguishes combustion upon the outer limits of the flame before every trace of combustible material is burnt; for it has been shown that small quantities of carbon monoxide, marsh gas, and even hydrogen escape unburnt from a gas flame.

The chemical decompositions which go on in the luminous area cannot be said to have been thoroughly established. It has been shown that very early in its passage up the flame, a certain amount of the marsh gas and ethylene present is converted into acetylene, the change taking place as the result of heat alone. The gases ascending the dark region *d* are surrounded on all sides by a wall of burning material, and are thereby raised in temperature to the point at which the marsh gas and ethylene suffer decomposition into acetylene and hydrogen—

$$2CH_4 = C_2H_2 + 3H_2.$$

The following table (Lewes) shows the gradual development of acetylene in such a flame :—

| | Total Unsaturated Hydrocarbons. Per Cent. | Acetylene Per Cent. |
|---|---|---|
| Gas in burner . . . . | 4.38 | 0.035 |
| ½ inch above rim of burner . . | 4.00 | 0.340 |
| 1½ inches above rim . . . | 1.53 | 0.560 |
| Tip of dark region . . . | 1.98 | 1.410 |
| Centre of luminous area . . | 0.45 | 0.045 |
| Tip of luminous area . . . | 0.00 | 0.00 |

Therefore, by the time the gases have reached the tip of the dark region, the effect of heat upon them has been to raise the amount of acetylene to over 70 per cent. of the total unsaturated hydrocarbons present. As the acetylene and other hydrocarbons pass on through the flame, along with steam, carbon dioxide, and carbon monoxide, other and more complex changes go on, whereby denser hydrocarbons are formed, and carbon itself is precipitated.

The formation of acetylene in that region of the flame where the coal gas is in excess, is well exemplified in the case of air burning in an atmosphere of coal gas (see Fig. 71). In this flame, the air is in the inside and the coal gas upon the outside; it is, in effect, an ordinary coal gas flame *turned inside out.* The formation of acetylene, instead of taking place *within* the flame (in which case it has to pass through the heated area, and is thereby decomposed), takes place upon the outer surface or periphery of the flame, and therefore largely escapes combustion and decomposition, and passes away into the coal gas atmosphere. (See Acetylene, where this method is described for the preparation of this compound.)

**The Cause of Luminosity in Flames.**—The light-giving property of a flame is not due to the operation of any one simple cause. It was at one time supposed, that the luminosity of a flame depended solely upon the presence in it of suspended solid matter, resulting from the chemical decompositions going on during combustion. It has been shown, however, that this general statement does not satisfy all cases, as there are a number of highly luminous flames in which, from the known properties of the products of combustion, there cannot possibly be any solid matter present. Thus, for example, phosphorus burning in air gives a flame of a high degree of luminosity; but the phosphorus pentoxide which is the product of combustion, although solid at ordinary temperatures, is volatile at a temperature far below that of the flame. The same may be said of the luminous flame of arsenic burning in oxygen, where the still more volatile arsenious oxide is the product.

When carbon disulphide burns in oxygen or in nitric oxide, a well-known and intensely luminous flame is obtained, in which only gaseous products of combustion can be present; and, lastly, the flame of hydrogen burning in oxygen, can be made under certain circumstances to emit a bright light: thus, when a mixture of these gases is ignited in a closed eudiometer, their combustion is attended with a brilliant flash of light, the only product being water.

There are three causes which may operate, either separately or together, in imparting luminosity to a flame, or in increasing its light-giving power: these are—1. The temperature of the flame. 2. The density of the flame gases, and 3. The introduction into the flame of solid matter. These three causes will be treated separately, and illustrations given, which, so far as our knowledge extends, can be directly traced to the independent operation of each.

1. The effect of temperature.

(*a*.) Upon flames in which solid matter is known to be absent.

When phosphorus is introduced into chlorine, it spontaneously inflames and burns with a flame of such extremely feeble luminosity that it may be regarded as non-luminous; if, however, the chlorine be previously strongly heated by being passed through a red hot tube, and the phosphorus be boiling when it comes in contact with the gas, the combustion thus started upon a higher platform of temperature is accompanied by a flame of very considerable luminosity.

The flame of carbon disulphide burning in air emits but a feeble light; but when this substance burns in pure oxygen, its temperature of combustion is greatly raised, and the luminosity of the flame is enormously increased.

Phosphoretted hydrogen burning in air gives a flame of considerable luminosity; but when this flame is fed with pure oxygen, and its temperature thereby raised, it becomes intensely luminous.

(β.) Upon flames in which solid matter is known to be present.

The flames produced by the combustion of zinc or magnesium in the air, and in which the solid oxides are present, have their luminosity greatly increased when pure oxygen is substituted for air, and the temperature of combustion thereby augmented.

The same result is seen in the case of flames in which the solid matter is artificially introduced, as in the familiar Welsbach burner, where a solid gauze mantle, composed of an alkaline earth, is placed in the flame-cone of a non-luminous gas flame, thereby rendering it luminous. If the temperature of this flame be augmented by feeding it with oxygen, the light emitted by the incandescent solid is greatly increased.

(γ.) Upon flames in which solid matter is believed to be present, such as candle, gas, and other hydrocarbon flames.

When a candle or gas flame is introduced into oxygen, although it shrinks in size, its luminosity is increased. It has also been shown that when a coal gas flame is chilled, by causing it to spread against a cold surface, its luminosity is diminished or destroyed altogether; and, conversely, if the gas and the air supplying the flame be strongly heated before combustion, the luminosity is greatly increased. In this case, however, the direct effect of change of temperature is complicated by the decompositions going on in the flame; for, as already mentioned, the conversion of the non-illuminating marsh gas into the highly illuminating gas acetylene, is a function of the temperature.

The increase of light obtained from a gas flame by previously heating the gas and air, is the principle underlying all the so-called *recuperative* burners.

It is evident, therefore, that most flames gain luminosity by having their temperature raised. There are, however, cases in which increase of temperature *alone* appears to exert no influence upon the luminosity. The flame of hydrogen, for example, which is practically non-luminous when burning in air, does not become more luminous when burnt in oxygen, although its temperature is greatly increased.

2. The influence of the density of the flame gases.

It has been shown by Frankland * that the luminosity of flame is intimately associated with the pressure to which it is subjected, or with the density of the flame gases. Thus, it is found that a gas or candle flame, when burnt either at high altitudes, or in artificially rarefied atmospheres, has its luminosity greatly reduced; and, *per contra*, when caused to burn under increased pressure, the luminosity is increased. In the case of hydrocarbons, complication arises from the fact, that the temperature of the flame is changed by alterations of pressure. Under diminished pressure the temperature falls, and although there is less loss of heat by radiation in rarefied air, than in air at the ordinary pressure, it is possible that the general lowering of the temperature of the flame, may modify the chemical decompositions in the direction already referred to.

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* Phil. Trans., vol. cli. p. 629; Proc. Royal Society, vol. xvi. p. 419.

Flames other than those of hydrocarbons, however, and in which no solid matter can exist, are found to become luminous when the density of the flame gas is increased by pressure. Thus, the flame of carbon monoxide in oxygen at ordinary pressures, emits a moderate light; but when exposed to a pressure of two atmospheres the luminosity is greatly increased. Even the non-luminous flame of hydrogen burning in oxygen, becomes luminous under a pressure of two atmospheres, and when examined by the spectroscope is found to give a continuous spectrum. It has been found, as a general rule, that dense gases and vapours, when heated, become incandescent, or luminous, at much lower temperatures than those of low specific gravity; thus, if different gases be raised to incandescence by the passage through them of electric sparks, under similar conditions, it is seen that the light emitted by the glowing vapour, varies with the density of the gas. The luminosity of glowing oxygen (density, 15.96) is greatly superior to that of hydrogen (density, 1), while the light emitted when the sparks are passed through chlorine (density, 35.5) is considerably in advance of either. And it is found that in one and the same gas, the luminosity of the spark increases as the density is increased by artificial compression. Other things being equal, it may be said that the denser the vapours which are present, the more luminous is the flame.

FIG. 82.

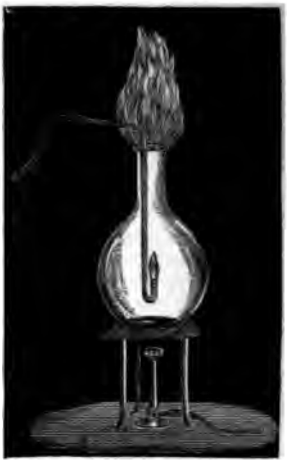

FIG. 83.

3. The introduction of solid matter into flames.

Non-luminous flames may be rendered luminous by the intentional introduction into them of solid matter, which, by being raised to a sufficiently high temperature, will become strongly incandescent. Thus, the ordinary lime-light owes its luminosity to the incandescence of the fragment of lime, which is raised to a bright white heat by the high temperature of the non-luminous oxy-hydrogen flame. The lime is not vaporised at the temperature of the flame, the light being entirely due to the glowing solid matter.

The "Welsbach" burner, already referred to, is another example of the same order, the luminosity in this case being due to the introduction into an ordinary non-luminous Bunsen flame, of a fine gauze mantle made of alumina or other metallic oxide (Fig. 82). When such a mantle is raised to incandescence by the heat of the gas flame, it emits a bright white light, strongly resembling that of an ordinary Argand gas flame. A flame may also be rendered luminous by the intentional precipitation within it of carbon, which, by its ignition and its combustion, produces a high degree of luminosity: thus, if a small quantity of alcohol be boiled in a flask, and a jet from which chlorine is issuing be then lowered through the burning vapour into the flask, as shown in Fig. 83, the chlorine will burn in the alcohol vapour with a luminous flame; and the precipitated carbon (which is thrown out of combination by the action of the chlorine upon the alcohol) ascending into the previously non-luminous alcohol flame will render it brightly luminous.

From these considerations it will be evident that the luminosity of a flame may be due, first, to the presence of vapours sufficiently dense to become incandescent at the temperature of the flame; or, second, to the presence of solids rendered incandescent, either by the heat of the flame gases alone, or in conjunction with their own combustion; or, third, from the simultaneous operation of all these causes. Ordinary gas and candle flames come under the last of these heads. The decompositions that go forward in these flames, not only give rise to dense vapours which become incandescent, but also to the precipitation of solid carbon, which by its ignition and combustion adds to the luminosity of the flame.

**The Bunsen Flame.**—The construction of the Bunsen lamp is too well known to need description. The gas, issuing from a small jet situated at the base of a metal tube, and mixing with air which is drawn in through openings in the tube, burns at the top of the chimney with the familiar non-luminous flame. The existence of this flame in its ordinary condition depends upon two main causes; first, upon the fact that in the immediate neighbourhood of a jet of gas issuing from a small orifice, there is a reduction of pressure; and, second, upon the relation between the velocity at which the gases pass up the tube, and the rate of propagation of combustion in the mixture of air and coal gas. Upon the first of these causes depends the entrance of air into the "air-holes" of the lamp, and upon the second depends the continuance of the flame in its position upon the top of the tube.

As the coal gas issues from the small jet at the base of the chimney, instead of the gas escaping through the side-holes, air is drawn into the tube by virtue of the reduced pressure produced immediately round the jet. That this area of reduced pressure actually exists in the neighbourhood of the jet of a Bunsen, may be proved by attaching a delicate manometer to the air-hole of such a lamp, as shown in Fig. 84. As the gas is turned on, the liquid in the horizontal tube will be sucked towards the lamp, showing that the issuing gas causes a partial vacuum in its immediate neighbourhood.*

In order that the flame shall remain at the top of the tube, there must be a certain relation between the velocity of the issuing gases, and the rate of propagation of combustion in the mixture; for if the latter be greater than the former, the flame will travel down the tube and ignite the gas at the jet below. By gradually reducing the supply of gas to the flame, and so altering the proportion of gas and air ascending the tube, the mixture becomes more and more explosive, until a point is reached when the velocity of inflammation is greater than the rate of efflux of the gases, and the flame travels down the tube, and the familiar effect of the flame "striking down" is obtained.

The same result may be brought about, and the effect more closely observed, by extending the chimney of the lamp by means of a wide glass tube. As the supply of gas is reduced, or the quantity of air introduced is increased, the flame will be seen to shrink in size and finally descend the tube. By adjustment it may be caused either to explode rapidly down the tube, or to travel quite slowly, or even to remain stationary at some point in the tube which is slightly constricted, and where, therefore, the flow of the issuing gas is slightly accelerated.†

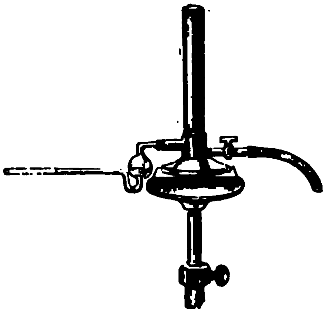

FIG. 84.

The non-luminosity of a Bunsen flame is due to the combined operation of three causes, namely, oxidation, dilution, and cooling. It was formerly supposed that the destruction of the luminosity of a gas flame, by the admixture of air with the gas before burning, was entirely owing to the influence of the oxygen in bringing about a more rapid and complete state of oxidation, that the hydrocarbons were at once completely burnt up by the additional supply of oxygen so provided. It has been shown, however, that not only is this effect brought about by air, but also by the use of such inert gases as nitrogen, carbon dioxide, and even steam. The following table (Lewes) shows the relative volumes of various gases that are required to destroy the luminosity of a gas flame:—

| | | | | | |
|---|---|---|---|---|---|
| 1 volume | of coal gas | requires | 0.5 | volumes | of oxygen. |
| ,, | ,, | ,, | 1.26 | ,, | carbon dioxide. |
| ,, | ,, | ,, | 2.27 | ,, | air. |
| ,, | ,, | ,, | 2.30 | ,, | nitrogen. |
| ,, | ,, | ,, | 5.11 | ,, | carbon monoxide. |

That the atmospheric oxygen effects the result by a direct oxidising action, and is not acting merely as nitrogen does, is proved by the fact, that mixtures of oxygen and nitrogen containing a higher proportion of oxygen than is present in air, destroy the luminosity more rapidly than is effected by air. Thus, when mixtures containing nitrogen and oxygen in the proportion of 3 to 1, 2 to 1, 1 to 1 by volume are employed, the volumes of the mixtures required to destroy the luminosity of one volume of coal gas, are respectively 2.02, 1.49, and 1.00.

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* See "Chemical Lecture Experiments," 480-484.

† Ibid., 448.

It has been shown that when coal gas is diluted with nitrogen, a higher temperature is necessary to effect its decomposition; hence the action of the atmospheric nitrogen in causing the loss of luminosity of a gas flame, is in part due to the higher temperature that is required for the formation of acetylene, which, as already mentioned, is the first step in the decomposition and condensation of the hydrocarbons in the gas.

As already mentioned, the luminosity of a flame is very much influenced by alterations of temperature; and just as the non-luminosity of the outer mantle of an ordinary flame, is partly due to the cooling action of the air which is dragged into the flame from the outside, so the want of luminosity of the Bunsen flame, is in part due to the cooling influence of the large volume of air that is drawn up into the interior of the flame. That the gases which are drawn into a flame reduce the luminosity by virtue of their cooling action, is borne out by the fact, that the higher the specific heat of the diluent (and therefore the greater its power to abstract heat from the flame) the less of it is required to effect the destruction of the luminosity; thus, as already mentioned, less carbon dioxide than nitrogen is necessary to render a flame non-luminous: the specific heat of nitrogen is 0.2370, while that of carbon dioxide is 0.3307.

The specific heat of oxygen is also slightly greater than that of nitrogen, being 0.2405; but the cooling effect of dilution with this gas, is enormously overpowered by the increased temperature due to its oxidising action upon the combustible materials of the flame.

Experiments made upon the actual temperatures of various regions of a Bunsen flame, rendered non-luminous by admixture with different gases, the results of which are seen in the following table (Lewes), show the cooling effect of these diluents upon the flame:—

*Temperature of Flame from Bunsen Burner, burning* 6 *cubic feet of Coal Gas per Hour.*

| Region in Flame. | Luminous Flame. | Flame rendered Non-luminous by | | |
|---|---|---|---|---|
| | | Air. | Nitrogen. | Carbon Dioxide. |
| | Degrees. | Degrees. | Degrees. | Degrees. |
| ½ inch above burner . . . . | 135 | 54 | 30 | 35 |
| 1½ inch above burner . . . . | 421 | 175 | 111 | 70 |
| Tip of inner cone . . . . | 913 | 1090 | 444 | 393 |
| Centre of outer cone . . . . | 1328 | 1533 | 999 | 770 |
| Tip of outer cone . . . . | 728 | 1175 | 1151 | 951 |
| Side of outer cone, level with tip of inner cone . . . . | 1236 | 1333 | 1236 | 970 |

In the case of air, it will be seen that the first effect is to cool the flame; but in the upper region, where the oxidising action of the oxygen is felt, the temperature rapidly rises to a maximum at a point about half way between the tip of the inner and outer cones. In the flames rendered non-luminous by the two inert gases, the highest temperature is only reached at the outer limit, where the full amount of oxygen for combustion is obtained from the outer atmosphere.

On account of the wide range of temperature exhibited by the various regions of a Bunsen flame, it constitutes a most valuable analytical instrument, for by the judicious use of the different parts of the flame, it is often possible to detect the presence of several flame-colouring substances in a mixture. Thus, if a mixture of sodium and potassium salts be introduced upon platinum wire into the cooler region of the flame near its base, the more volatile potassium compound will impart its characteristic violet tint to the flame, before the sodium salt is volatilised sufficiently to mask the colour, by the strong yellow it itself gives to the flame. In this way many mixtures may readily be differentiated.

If a piece of copper wire be held horizontally across a Bunsen flame, so as to cut the inner cone, it will be seen that the wire in contact with the edges of the flame becomes coated with copper oxide, while the portion in the centre remains bright. On moving the wire so as to bring the oxidised portion into the inner region, the oxide will be reduced, the metal once more becoming bright. The outer area of a flame, where oxygen is in excess, is called the *oxidising flame;* while the inner region, in which heated and unburnt hydrogen or hydrocarbons exist, is spoken of as the *reducing flame.* These regions exist in all ordinary flames. The oxidising action of the outer flame of a candle, for example, is illustrated in the behaviour of the wick. So long as the wick remains in the inner region of the flame it is not burnt; and in the early days of candles, as the tallow gradually consumed, the wick remained standing straight up, and by degrees extended into the luminous area of the flame, where, owing to the deposition of soot upon it, it frequently developed a cauliflower-like accretion, which greatly impaired the luminosity of the flame, and which necessitated the use of snuffers. In the modern candle, owing to a method of plaiting the wick, it is caused to bend over (as shown in Fig. 79), and so thrusts its point into the oxidising region, where it is continually burnt away.

# PART III

## THE SYSTEMATIC STUDY OF THE ELEMENTS, BASED UPON THE PERIODIC CLASSIFICATION.

## CHAPTER I

### *THE ELEMENTS OF GROUP VII. (FAMILY B.)*

| | | | |
|---|---|---|---|
| **Fluorine, F** | 19.06 | Bromine, Br | 79.76 |
| **Chlorine, Cl** | 35.37 | Iodine, I | 126.54 |

THE first to be discovered, and the most important element of the group, is chlorine, which is a constituent of sea salt (sodium chloride). The term *halogen*, signifying sea salt producer, has been applied to this family of elements, on account of the close resemblance between their sodium salts and sea salt. This family exhibits, in a marked manner, many of the features which are found to exist in most chemical families of elements.

In their general behaviour they strongly resemble one another, and readily displace each other in combinations without producing any very marked change upon the character of the compounds. They each unite with hydrogen, giving rise respectively to hydrofluoric acid, $HF$; hydrochloric acid, $HCl$; hydrobromic acid, $HBr$; hydriodic acid, $HI$.

These hydrogen compounds are all colourless gases, which fume strongly in the air; they are extremely soluble in water, and are strongly acid in character. In combination with potassium and with sodium, the halogens form a series of compounds, which are similarly constituted, and which closely resemble each other in their habits. Their similarity of composition is expressed in the following formulæ—

Compounds with potassium, $KF$, $KCl$, $KBr$, $KI$.
*Compounds with sodium*, $NaF$, $NaCl$, $NaBr$, $NaI$.

The physical properties of the elements, exhibit a regular gradation with increasing atomic weight; thus, fluorine and chlorine are gases, bromine is liquid, while iodine is solid, at ordinary temperatures. In their chemical activity they also show the same gradual change; thus, in the case of their combination with hydrogen, when fluorine and hydrogen are brought together, combination instantly takes place with explosion, even in the dark. Chlorine and hydrogen do not combine in the dark, but in diffused daylight they unite slowly, and in direct sunlight their combination takes place suddenly with explosion.

Bromine vapour and hydrogen do not combine even in direct sunlight, but a mixture of the two gases ignites in contact with a flame, yielding hydrobromic acid, while iodine vapour and hydrogen require to be strongly heated in contact with spongy platinum to effect their combination. This difference in the activity of the halogens towards hydrogen, is seen by a comparison of the heats of formation of their hydrogen compounds, thus—

$$\begin{array}{llll} H + Cl & = HCl & + \ 22{,}000 & \text{cal. (Thomsen).} \\ H + Br & = HBr & + \ \ 8{,}440 & \text{,, } * \\ H + I & = HI & - \ \ 6{,}040 & \text{,, } \dagger \end{array}$$

The heat of formation of hydrofluoric acid has not yet been determined, but there can be no doubt that it is considerably greater than that of hydrochloric acid.

Although a strong resemblance exists between all the members of the halogen family, the element fluorine, which is the *typical* member (see p. 100), stands marked off from the others in many of its attributes. Thus fluorine exhibits a great tendency to form double salts which have no counterpart among the compounds of the other elements of the family, and at temperatures below 32°, the molecule of hydrofluoric acid consists of two atoms of hydrogen and two of fluorine, having the composition $H_2F_2$.

## FLUORINE.

Symbol, F. Atomic weight = 19.06.

**History.**—This element, the first of the halogen series, was the most recent to be discovered, it having baffled all attempts to

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[*] This value refers to bromine in the liquid state.

[†] Iodine as solid.

isolate it until the year 1886, when Moissan succeeded in solving the problem.

**Occurrence.**—Fluorine occurs in considerable quantities in combination with calcium in the mineral *fluor spar* ($CaF_2$), which is found in cubical crystals. On account of the occurrence of this mineral in large quantities in Derbyshire it is frequently termed *Derbyshire spar.* It is a constituent also of *cryolite*, $Na_3AlF_6$, *fluor-apatite*, $3P_2O_8Ca_3,CaF_2$, and many others. In small quantities fluorine is found in bones, in the enamel of teeth, and also in certain mineral waters.

**Mode of Formation.**—When an electric current is passed into an aqueous solution of hydrochloric acid, the acid is decomposed into its elements, chlorine being liberated at the positive electrode, while hydrogen is evolved at the negative. When aqueous hydrofluoric acid is treated in the same way, the water only is decomposed, oxygen and hydrogen being liberated. Davy found that the more nearly the acid approached the anhydrous condition, the less easily did it conduct electricity; and that in the perfectly pure state, that is, entirely free from water, hydrofluoric acid was a non-conductor. Moissan's recent success in the isolation of fluorine, depends upon the discovery that a solution of the acid potassium fluoride, HF,KF, in anhydrous hydrofluoric acid is an electrolyte, and that by the passage of an electric current through this solution, fluorine is disengaged at the anode, or positive electrode, and hydrogen is evolved at the cathode.

The primary decomposition taking place is the breaking up of the acid potassium fluoride—

$$HF,KF = F_2 + H + K.$$

The atom of potassium, in contact with the free hydrofluoric acid present, is then converted into potassium fluoride with the elimination of an equivalent of hydrogen—

$$K + HF = KF + H.$$

And the normal potassium fluoride then unites with a molecule of the acid, to regenerate the acid salt—

$$KF + HF = HF,KF.$$

The reaction is performed in a U-tube made of an alloy of platinum *and iridium, a material* which is less acted upon by the liberated fluorine than platinum alone. The apparatus has two side-tubes (Fig. 85), which can be either closed with a screw cap, C, or connected to platinum delivery tubes by means of the union D. The two limbs of the tube are closed by means of stoppers made of fluor spar, shown in section at S, and which can be securely screwed into the tube. These serve to insulate the electrodes, which are constructed of the same platinum-iridium alloy. They are made thick at the ends, as seen in the figure, for even this alloy is soon acted upon by the fluorine as it is evolved at the anode. The anhydrous hydrofluoric acid is introduced into the apparatus, and about 25 per cent. of its weight of the acid potassium fluoride is added, which readily dissolves in the liquid. As hydrofluoric acid is an extremely volatile liquid (boiling at 19.4), it is necessary that the platinum apparatus containing it should be artificially cooled; for this purpose it is immersed in a glass vessel containing methyl chloride, M (Fig. 86). The boiling-point of this liquid is −23°, but by connecting the tube C to an aspirator, and causing a current of air to circulate through the apparatus, the temperature of the liquid may be lowered to −40°, or −50°. The methyl chloride is continuously replenished from the reservoir B. In order to prevent the deposition of moisture upon the glass vessel M, it is placed within the glass jar A, containing a few lumps of calcium chloride in order to dry the contained air. On passing a current from 20 to 25 Grove's cells through the apparatus, fluorine is evolved at the positive electrode, and hydrogen is liberated at the negative.*

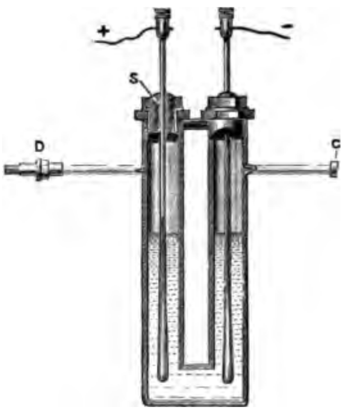

FIG. 85.

**Properties.**—Fluorine is, of all known elements, the most chemically active. It is on account of its intense chemical affinities that it so long resisted all attempts to isolate it, as when liberated from combination it instantly combined with the materials of the vessels in which the reactions are made. It is impossible to collect this gas by any of the usual methods, for it decomposes water, and instantly combines with mercury. It also attacks glass, so that it can only be collected by displacement of air, in vessels of platinum. Fluorine appears to be a colourless gas, judged by the small volume of it that can be viewed at once. The smell of the gas is very characteristic, it is irritating to the mucous membranes, and is not unlike the odour of the mixture of chlorine and chlorine monoxide, evolved from potassium chlorate and hydrochloric acid. Whether the smell actually perceived is the true smell of fluorine is doubtful, for when fluorine comes into contact with the moisture in the nostrils, water is decomposed, with the formation of ozonised oxygen and hydrofluoric acid.

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* Fluorine has recently been obtained by Brauner (June 1894) by heating potassium fluorplumbate, $3KF,HF,PbF_4$. At 200° this salt gives off *hydrofluoric* acid, HF, and when heated to 230°-250° fluorine is evolved.

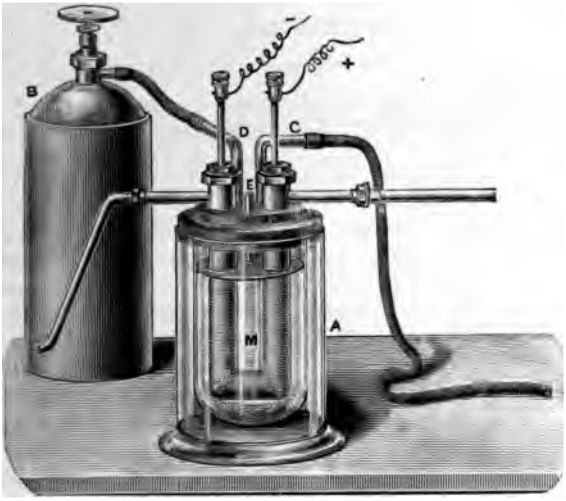

FIG. 86.

Fluorine not only decomposes potassium iodide, with liberation of iodine, but also displaces chlorine from sodium chloride.

It combines directly with a large number of elements with intense energy; in contact with hydrogen it instantly explodes.

Iodine, sulphur, and phosphorus first melt, and then take fire in fluorine. Crystals of silicon when brought into the gas, spontaneously inflame, and burn with brilliancy. All of the metals are acted upon by fluorine; some, when finely divided, undergoing spontaneous inflammation when thrown into the gas. Even gold and platinum are attacked by fluorine, especially if gently warmed; its action upon the latter metal being seen by the corrosion of the apparatus, and especially the positive electrode employed in its preparation.

Organic compounds are attacked by fluorine with violence, and often inflamed.

### HYDROFLUORIC ACID.

Formula, $H_2F_2$ and HF. Molecular weight, 40 and 20. Density, 20 and 10.

**Modes of Formation.**—(1.) Hydrofluoric acid is produced when powdered calcium fluoride (fluor spar) is acted upon by strong sulphuric acid—

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

This method is employed for the commercial preparation of aqueous solutions of hydrofluoric acid. The mixture of fluor spar and sulphuric acid is gently warmed in a leaden retort, and the gaseous acid passed into water contained in leaden bottles. This aqueous acid is sent into the market in gutta-percha bottles.

(2.) The anhydrous acid is prepared by heating hydrogen potassium fluoride (acid potassium fluoride) in a platinum retort. The double fluoride of potassium and hydrogen, splits up into normal potassium fluoride, and hydrofluoric acid—

$$HF,KF = KF + HF.$$

For this purpose the perfectly dry double fluoride is placed in a platinum retort, which is screwed to a platinum condensing arrangement, as seen in Fig. 87. The wooden trough through which the long tube passes is filled with a freezing mixture, and the platinum bottle is also surrounded by a similar mixture.

**Properties.**—Anhydrous hydrofluoric acid is a colourless, limpid, strongly fuming liquid, which boils at 19.5°. It has a powerful affinity for water, and can only be preserved in perfectly stoppered platinum vessels, which are kept in a cool place. The acid at once attacks gutta-percha. Gore found that the anhydrous acid was without action upon glass.

ure hydrofluoric acid is an extremely dangerous substance to ıipulate; its vapour, even when diluted with air, has a most ating and injurious effect upon the respiratory organs, and if ıled in the pure state causes death.

. single drop of the liquid upon the skin, causes the most painful rated sores, accompanied by distressing aching pains throughthe whole body. The metals potassium and sodium dissolve in hydrofluoric acid, with the formation of fluorides and evolution ydrogen.

he vapour density of hydrofluoric acid at a temperature of 32°, esponds to the formula $H_2F_2$. As the temperature is raised,

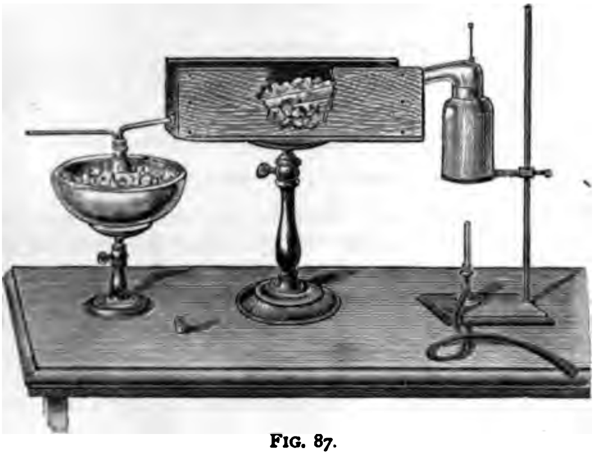

FIG. 87.

ıe density of the vapour falls steadily, until at 88° it is 10, a density hich is normal for the formula HF. The composition of this compound, therefore, as ordinarily seen, is probably represented by the ɔrmula $H_2F_2$, the molecules of which undergo dissociation when he temperature rises, until at 88° the substance consists entirely f the simpler molecules HF.

Gaseous hydrofluoric acid rapidly attacks glass, and it is largely mployed for etching purposes, both for obtaining designs upon lass, and for the purpose of etching graduations upon glass measuring instruments. The object to be etched, is first coated with ax, and the design or other marks cut upon the wax by means of a pointed steel tool. In this way the surface of the glass is laid bare in parts, and on exposing the object to the action of the acid, either as gas or aqueous solution, the glass is rapidly eaten into, where the surface has been exposed. Its action upon glass is due to the readiness with which it attacks silicates, the fluorine combining with the silicon to form silicon tetrafluoride—

$$SiO_2 + 4HF = 2H_2O + SiF_4.$$

Hydrofluoric acid is extremely soluble in water, forming a strongly acid corrosive liquid, which readily dissolves many of the metals with evolution of hydrogen—

$$Fe + 2HF = FeF_2 + H_2.$$

Silver and copper are also dissolved by this acid.

The fluorides of the alkaline metals and of silver are soluble in water.

### CHLORINE.

Symbol, Cl. Atomic weight, 35.37. Molecular weight, 70.74.

**History.**—Chlorine was discovered by Scheele (1774), but was regarded by him as a compound substance. He applied to it the name of *dephlogisticated marine acid air*, having obtained it by the action of hydrochloric acid upon ores of manganese. The belief that chlorine was a compound of oxygen and hydrochloric acid, was generally held until Davy's time, and gave rise to the name of *oxymuriatic acid*.

The elementary nature of chlorine was proved by Davy (1810) who gave to it the name *chlorine*, in allusion to the greenish-yellow colour of the gas.

**Occurrence.**—In the uncombined condition chlorine does not occur in nature. In combination with metals, as chlorides, chlorine is very abundant, the commonest chloride being sodium chloride (common salt).

Many of the salts found in the Stassfurt deposits, consist largely of chlorides (see Alkali Metals). Chlorides of the alkali metals are also found in animal secretions and in certain plants. Chlorine occurs in combination with hydrogen, as hydrochloric acid, in volcanic gases, and also in the gastric juice.

**Modes of Formation.**—(1.) When hydrochloric acid is poured upon manganese dioxide, and the mixture kept cool, a dark-brown n is obtained, which rapidly decomposes at a slight rise of rature with the evolution of chlorine.

as not yet been clearly established whether this brown solu- nsists of the compound $MnCl_4$ or $Mn_2Cl_8$, formed according of the equations—

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O.$$

$$2MnO_2 + 8HCl = Mn_2Cl_8 + Cl_2 + 4H_2O.$$

this dark-brown solution is gently warmed, the higher le breaks up into manganous chloride ($MnCl_2$) and chlorine; mplete reaction being expressed by the equation—

$$MnO_2 + 4HCl = 2H_2O + MnCl_2 + Cl_2.$$

xperiment is conveniently carried out in the apparatus seen . 88. The mixture of manganese dioxide and hydrochloric

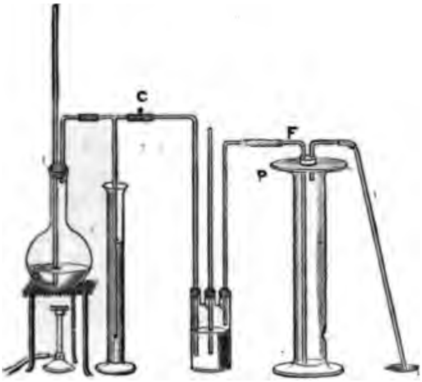

FIG. 88.

is gently heated in a large flask, and the gas, after being d through water in the Woulf's bottle, may be collected by ward displacement, as shown in the figure.*

Instead of employing hydrochloric acid, the materials from this compound is prepared, namely, sodium chloride and uric acid, may be used. Thus, if a mixture of sodium chloride, manganese dioxide, and sulphuric acid be gently warmed chlorine is readily evolved—

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* See *Experiment 149*, "Chemical Lecture Experiments."

$$2NaCl + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$$

It will be seen that by this reaction the whole of the chlorine contained in the reacting compounds is evolved as gas, while in the former case a part of it remains in combination with the manganese.

(3.) Many other highly oxygenised compounds, when acted upon by hydrochloric acid, evolve chlorine; thus, when crystals of potassium bichromate are drenched with hydrochloric acid, and the mixture heated, a rapid stream of chlorine takes place, thus—

$$K_2Cr_2O_7 + 14HCl = 2KCl + Cr_2Cl_6 + 7H_2O + 3Cl_2$$

(4.) When crystals of potassium chlorate are similarly treated, a mixture of chlorine and chlorine peroxide is evolved, even without the application of heat—

$$4KClO_3 + 12HCl = 4KCl + 6H_2O + 3ClO_2 + 9Cl.$$

(5.) Red lead ($Pb_3O_4$), when treated with hydrochloric acid, reacts in a manner similar to manganese dioxide and many other peroxides. In the case of lead, however, there is no intermediate chloride formed—

$$Pb_3O_4 + 8HCl = 3PbCl_2 + 4H_2O + Cl_2$$

(6.) **Manufacturing Processes — Deacon's Process.**—This method for the preparation of chlorine, is by the oxidation of the hydrogen in hydrochloric acid by *atmospheric* oxygen. It will be seen that in the foregoing methods the oxidation of this hydrogen is carried on at the expense of the oxygen contained in either the metallic peroxide, or the highly oxygenated salt used; in the Deacon process atmospheric oxygen is made use of. When a mixture of gaseous hydrochloric acid and oxygen is heated, a slight decomposition takes place; but if these gases be heated in the presence of a third substance, which acts as a catalytic agent, the decomposition of the hydrochloric acid is much more readily effected. The catalytic agent employed in the Deacon process is cuprous chloride ($Cu_2Cl_2$). This substance is capable of taking up tional quantity of chlorine, and of being converted into loride ($CuCl_2$), thus—

$$Cu_2Cl_2 + Cl_2 = 2CuCl_2.$$

refore, a mixture of hydrochloric acid and oxygen be over fragments of pumice impregnated with cuprous contained in a tube which is heated to dull redness, the loric acid will be decomposed. We may suppose that the of oxygen for the hydrogen in hydrochloric acid, is un- overcome the affinity existing between the hydrogen and , but that the additional pull exerted upon the molecules chloric acid by the cuprous chloride, is sufficient to dis- equilibrium and rupture the molecule—

$$O \leftarrow \begin{array}{c|c} H & Cl \\ H & Cl \end{array} \rightarrow Cu_2Cl_2.$$

sult of the action being $H_2O + 2CuCl_2$.

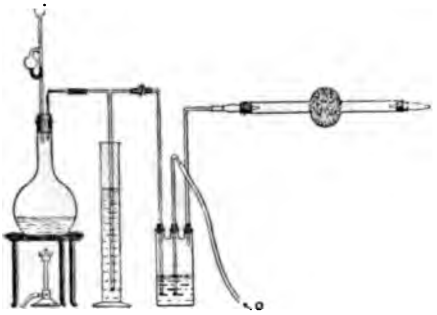

FIG. 89.

temperature at which the reaction is carried on, however, pound $CuCl_2$ cannot exist; two molecules of it are con- nto one of $Cu_2Cl_2$, and a molecule of chlorine is evolved. l result, therefore, of the reaction may be thus expressed—

$$O + 2HCl + Cu_2Cl_2 = H_2O + Cl_2 + Cu_2Cl_2.$$

ity the action is rather more complex, there being an intermediate d formed by the combination of cuprous chloride with oxygen. This

oxychloride of copper then acts upon the hydrochloric acid as seen
following equations:—

$$(1)\ Cu_2Cl_2 + O = Cu_2OCl_2.$$
$$(2)\ Cu_2OCl_2 + 2HCl = 2CuCl_2 + H_2O.$$
$$(3)\ 2CuCl_2 = Cu_2Cl_2 + Cl_2.$$

This reaction may be made on a small scale by means
apparatus shown in Fig. 89. Hydrochloric acid is generated
salt and sulphuric acid in the flask, and a stream of the gas
through the Woulf's bottle, into which also enters a stre
oxygen. The mixed gases are then passed through the bul
containing fragments of pumice which have previously been

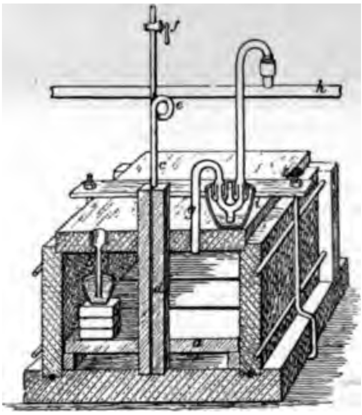

FIG. 90.

in a solution of cupric chloride, and dried. On heating the
means of a Bunsen flame, chlorine will issue from the end
tube. When chlorine is manufactured on an industrial sc
the Deacon process, the mixture of hydrochloric acid and
the proportion of four volumes of the latter to one volume of
chloric acid) is drawn by means of a Root's blower first t
iron pipes, which are heated to a temperature of about 50
then the hot gases pass on through the *decomposer*. This c
of a cylinder of cast iron, containing masses of broken b
burnt clay, impregnated with cupric chloride, and so arrang
the gases are drawn through the mass.

;as leaving the decomposer, consists of a mixture of chlorine, nposed hydrochloric acid, and atmospheric nitrogen and By passing them through water, the hydrochloric acid is l, and the chlorine is usually converted at once into bleach-der.

›rocess by which chlorine is usually made on a manufactur-le, is by the action of hydrochloric acid upon manganese The best ore for the purpose is pyrolusite. The process ıcted in stills made of thick slabs of stone, usually "York-ıg," which are fitted and luted together, and securely bound ·iron clamps. Fig. 90 shows such a chlorine still, repre-ıs cut across the centre.

:harge of *manganese* is placed upon the false bottom *a*, and l is run in through the funnel tube *b*, which, dipping into a ot, does not allow the gas to escape. As the action begins :en, steam is cautiously blown in from time to time. The : escapes by the pipe *g*, and passes from thence into the

reaction that goes on in the still, is the same as that given n the first mode of formation, except that as pyrolusite is e $MnO_2$, small quantities of other compounds are formed. lowing analyses, by Black, of *still-liquor* from stone stills, he general composition of this substance :—

| | |
|---|---|
| $MnCl_2$ | 10.5700 |
| $Al_2Cl_6$ | 0.6200 |
| $Fe_2Cl_6$ | 0.4551 |
| HCl (undecomposed) | 6.6220 |
| $H_2O$ | 81.7329 |
| | 100.0000 |

**The Weldon Process,** although indirectly a method for chlorine, is in reality a process for recovering the man-contained in the still-liquors as manganous chloride, and of :rting it into available manganese dioxide. The manganese ›vered, however, is again utilised for the preparation of e by the decomposition of a further quantity of hydrochloric The essence of the process is the following :—The *still-* s mixed with ground chalk, or limestone dust, in large tanks ı, and the mixture thoroughly stirred by agitators. One of ells, *A, is shown in the* diagrammatic figure. By this operation the free acid is neutralised, and the iron precipitated hydrated oxide. The neutral liquor, consisting of mangano chloride and calcium chloride, is then pumped into large tan where it is allowed to settle; one of these "settlers," B, is sho in the figure. By means of a pipe upon a swivel-joint, *f*, the cl liquid from the settler can be drawn off without disturbing t sediment, and run into the oxidiser C. The oxidiser is merel flat-bottomed iron cylinder, open at the top. Milk of lime fr

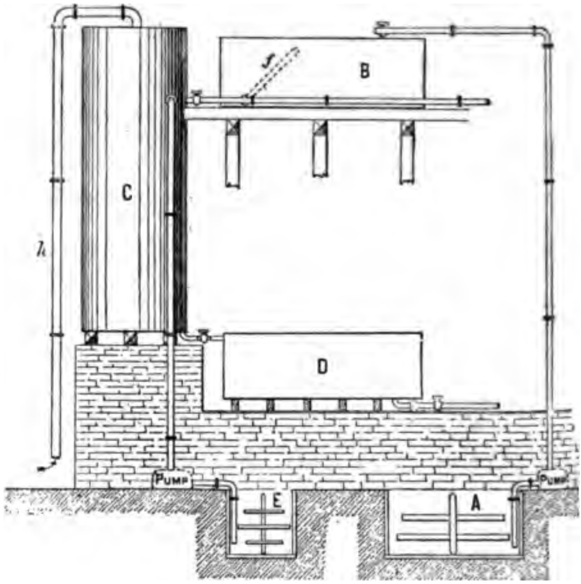

FIG. 91.

the tank E, where lime and water are stirred together, is pun into the oxidiser as required.

The milk of lime is added in quantity more than sufficie precipitate the manganese as manganous hydroxide, MnH Into this mixture, which consists of manganous hydroxide calcium hydroxide (milk of lime) in suspension, and to a sm extent in solution in the calcium chloride which is prese *stream of* compressed air is forced by means of the pipe *h*, w asses to the bottom of the oxidiser, where it ends in perforated ranches. During this process the manganese becomes oxidised, nd is converted mainly into calcium manganite, a compound of anganese dioxide with calcium oxide, $CaO,MnO_2$, or $CaMnO_3$. y a further addition of the neutral liquor from tank B, and by aising the temperature within the oxidiser by injecting steam, a ortion of the calcium manganite is converted into a compound aving the composition $CaO,2MnO_2$.

When the operation is complete, the contents of the oxidiser are run out into a series of tanks called *mud settlers*, of which one is shown at D in the figure. The product here settles as a thin black mud, known as the *Weldon mud;* and this is ultimately drawn from the settlers, and run direct into chlorine stills, where it is at once treated with hydrochloric acid for the preparation of chlorine. The Weldon stills are similar to the ordinary chlorine stills, but are much larger, and usually octagonal in shape.

**Properties.**—Chlorine is a greenish-yellow coloured gas, with a strong suffocating smell. It is quite irrespirable, and if inhaled in the pure state causes death. Even when largely diluted with air it is extremely disagreeable and injurious, as it acts rapidly upon the mucous membranes of the nose and throat, causing irritation and inflammation, which usually result in severe catarrh. A few bubbles of chlorine allowed to escape and diffuse into the air of a room, give to the air a distinct and rather pleasant smell. Chlorine is an extremely heavy gas, being $\frac{35.37}{14.44} = 2.45$ times heavier than air. One litre of the gas, measured under the standard conditions of temperature and pressure, weighs 3.168 grammes. The density of chlorine, taken at all temperatures, does not exactly agree with that which is required for the molecular formula $Cl_2$. At temperatures above 1200° the density is markedly less than theory demands, showing that partial dissociation of the chlorine molecules into single atoms has taken place. (Compare Bromine and Iodine.)

On account of its heaviness, chlorine is readily collected by displacement; it cannot be collected over mercury, as it attacks that metal, and in water it is considerably soluble. It may, however, be collected over a strong brine, as it is much less soluble in this solution than in water.

Chlorine is not inflammable, but it supports the combustion of many burning bodies. It is possessed of such extremely powerful chemical affinities that it acts upon a large number of substances at ordinary temperatures, and in many cases the combination is sufficiently energetic to result in the inflammation of the bodies. Phosphorus, when introduced into chlorine, first melts and then spontaneously inflames, burning with a somewhat feeble light to form phosphorus trichloride ($PCl_3$) and phosphorus pentachloride ($PCl_5$). The elements arsenic and antimony, when finely powdered and dusted into a vessel of chlorine, at once take fire and burn, forming their respective chlorides. Many metals, when finely divided, or in the form of thin leaf, such as ordinary Dutch metal, instantly take fire when brought into chlorine. If a quantity of sodium be heated in a deflagrating spoon until it begins to burn in the air, and be then plunged into chlorine, the sodium continues to burn in the gas with dazzling brilliancy, forming sodium chloride.

Although under ordinary circumstances chlorine unites with metals with great readiness, it has been shown that this action will not take place if the chlorine be absolutely dry. Thus, if chlorine which has been completely freed from aqueous vapour be passed into a tube containing bright metallic sodium, and the tube sealed, the sodium not only remains bright and unaffected by the gas, but may even be melted in the atmosphere of chlorine without any action taking place. Similarly, dry chlorine, when allowed to enter a flask filled with Dutch metal, has no action upon it ; but upon the introduction of the smallest trace of moisture, the metal at once takes fire.* These facts are of the same order as those mentioned in connection with oxygen, and have not yet received any satisfactory explanation.

Chlorine is not capable of direct combination with carbon ; ordinary combustibles, therefore, which consist of hydrocarbons, burn in chlorine by virtue of the combination of their hydrogen with the gas, and they burn with a lurid smoky flame, owing to the elimination of their carbon in the form of soot. A burning taper or ordinary gas flame, when introduced into chlorine, burns in this manner, emitting a dense smoke and forming fumes of hydrochloric acid.

Chlorine has a most powerful affinity for hydrogen ; a jet of hydrogen burns freely in chlorine, with the formation of hydrochloric acid. A mixture of hydrogen and chlorine unites with explosion on the application of a flame. This combination takes place also under the influence of light (see Hydrochloric Acid).

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* See Experiments 169, 170, "Chemical Lecture Experiments."

he affinity shown by chlorine for hydrogen is seen in its action pon many of the compounds of hydrogen and carbon. If one olume of ethylene ($C_2H_4$) be mixed with two volumes of chlorine, nd the mixture ignited, the carbon is instantly thrown out of combination as a black smoke, while the hydrogen unites with the hlorine, forming a cloud of hydrochloric acid. Similarly, if a quid hydrocarbon, such as turpentine ($C_{10}H_{16}$), be poured upon a iece of filter paper and the paper be thrust into a jar of chlorine, nstant inflammation takes place, with deposition of a large quantity f carbon.

Chlorine possesses strong bleaching properties, which depend pon its power of combining with hydrogen, for it is an essential ondition that water shall be present. The chlorine unites with he hydrogen of the water, and the liberated oxygen oxidises the olouring matter. If chlorine be bubbled into liquids coloured with any vegetable colouring matter, or if a dyed rag be dipped into hlorine water, the colour will be rapidly discharged. Ordinary writing-ink (which usually consists of a compound of iron with tannic and gallic acids) is readily bleached by chlorine; while printer's ink, which consists mainly of carbon, in the form of lamp-black, is not acted upon by this gas. If, therefore, a piece of printed paper be brushed over with writing-ink so as to completely obliterate the print, and the blackened paper be immersed in chlorine water, the writing-ink will be rapidly bleached away, leaving the print unchanged.

The bleaching power of chlorine constitutes its most valuable property from an industrial point of view; the chlorine for this purpose is combined with lime to form the substance known as bleaching-powder. (See Calcium Compounds.)

Chlorine is soluble in water to a considerable extent. One volume of water at 10° absorbs 3.0361 volumes of chlorine measured at 0° and under 760 mm. pressure. This solution, known as chlorine water, has the same colour as the gas, and smells strongly of chlorine. If exposed to the air, the chlorine rapidly diffuses out of the solution. Chlorine water cannot be preserved for any length of time, as it slowly undergoes decomposition, the chlorine combining with the hydrogen of the water, forming hydrochloric acid, which remains in solution, and the oxygen being liberated, thus—

$$H_2O + Cl_2 = 2HCl + O.$$

This action, which proceeds slowly under ordinary conditions, is greatly accelerated by the influence of light, and if exposed to direct sunlight the decomposition is very rapid.

If chlorine water be cooled to within one or two degrees of the freezing-point of water, or if chlorine be passed into ice-cold water, a solid crystalline compound of chlorine with water is deposited. This substance is termed *chlorine hydrate*, and has a composition expressed by the formula $Cl_2,10H_2O$. The compound is very unstable, and when exposed to the air it melts and rapidly gives off chlorine. If the crystals are quickly freed from adhering water, and are then sealed up in a glass tube, they may be heated to a temperature of 38° before being decomposed. Faraday made use of this compound in order to obtain liquefied chlorine. A quantity of the hydrate was sealed up in one limb of a bent tube and was gently warmed, the compound dissociated into water and chlorine, and the internal pressure caused the condensation of the chlorine to the liquid condition.

**Liquid Chlorine.**—Under the ordinary atmospheric pressure, chlorine may be liquefied by lowering its temperature to − 34°.

At a temperature of 0° the pressure required to effect its liquefaction is equal to six atmospheres. When, therefore, the liquid is obtained by heating the crystalline hydrate, as in Faraday's method, one limb of the tube should be cooled by being placed in ice.

The critical temperature of chlorine is 141°, and the pressure required to effect its liquefaction at that point, or its critical pressure, is 84 atmospheres. (See Liquefaction of Gases.)

Liquid chlorine has a bright golden yellow colour, entirely free from the greenish tint possessed by the gas. Its specific gravity is 1.33, and it boils at −33.6°. When cooled to a temperature of − 102, it freezes to a yellow crystalline mass. Liquid chlorine is now an article of commerce. It is contained in iron bottles lined with lead, and is largely exported in this form, for use in the extraction of gold, to parts of the world where the carriage of the plant and materials necessary for generating large quantities of chlorine, would be attended with great difficulties.

## HYDROCHLORIC ACID (*Hydrogen Chloride*).

Formula, HCl. Molecular weight = 36.37. Density = 18.185.

**History.**—In solution in water, this compound was known to the early alchemists, and the mixture of this solution with nitric acid constituted the valued liquid known as *aqua regia*. The preparation of hydrochloric acid from common salt is associated with the name of Glauber (1650), who obtained it by the action of sulphuric acid upon sodium chloride (common salt). Gaseous hydrochloric acid was first collected and examined by Priestley, who collected it over mercury, in the mercurial pneumatic trough invented by him. He named the gas *marine acid air*.

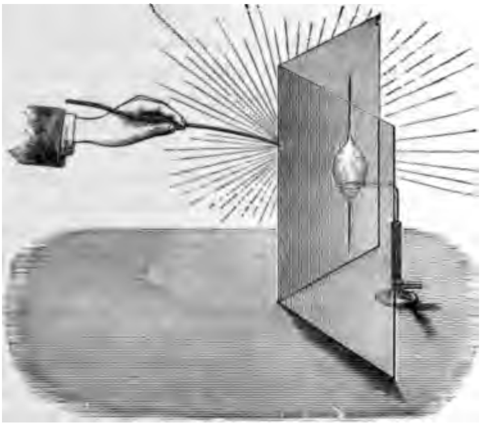

FIG. 92.

**Occurrence.**—Gaseous hydrochloric acid is evolved in considerable quantities from volcanoes during active eruption.

**Modes of Formation.**—(1.) Hydrochloric acid may be synthetically produced directly from its elements ; thus, this compound is formed when a jet of hydrogen is caused to burn in an atmosphere of chlorine. If a mixture of chlorine and hydrogen be ignited, the union takes place instantaneously with explosion, and hydrochloric acid is produced. The union of hydrogen with chlorine will also take place under the influence of light ; thus, if a mixture of these two gases be exposed to even diffused daylight for a few hours, the greenish colour imparted to the mixture by the chlorine will gradually disappear, and on examination it is found that the tube contains hydrochloric acid. This combination, which is only gradual when the mixture is exposed to diffused daylight, becomes explosively sudden if the mixed gases are exposed to direct sunlight, or any artificial light which is rich in rays of high refrangibility—the so-called *actinic* rays. If, therefore, a glass vessel be filled with a mixture of these gases in equal volumes, and the mixture be placed in bright sunshine, a violent explosion will result, and hydrochloric acid will be produced. This phenomenon is best illustrated by filling small thin glass bulbs with a mixture of the two gases obtained by the electrolysis of aqueous hydrochloric acid. The bulbs when filled can be hermetically sealed before the blowpipe without causing the combination of the gases,[*] and if kept in the dark may be preserved indefinitely.

On exposing one of these bulbs to the light of burning magnesium, the combination of the two gases instantly takes place, with a sharp explosion, which shatters the bulb to powder. The bulb should therefore be screened, as shown in Fig. 92.

The rays of light which are capable of causing this combination are those which compose the blue and violet end of the spectrum; if these particular rays are absorbed from the light by means of ruby glass, the mixture of gases may be exposed to the red light so obtained without any action taking place.[†]

The combination of chlorine with hydrogen is not attended by any alteration in volume; one volume of chlorine combines with one volume of hydrogen, and the resultant hydrochloric acid occupies two volumes. This may be readily proved by filling a stout glass tube, provided with a stop-cock at each end, with a mixture of the two gases in exactly equal volumes, and causing them to combine either by the influence of light, or by the passage of an electric spark by means of the platinum wires sealed into the tube (Fig. 93). On opening one of the stop-cocks under mercury, it will be seen that

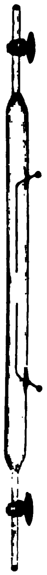

FIG. 93.

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[*] *See Experiment* 173, "Chemical Lecture Experiments."

[†] Ibid., p. 90.

no mercury is drawn in, neither does any gas pass out from the tube, thus showing that the union has taken place without any alteration in the volume. If one of the cocks be now opened beneath water, the hydrochloric acid which has resulted from the union of the hydrogen and chlorine, being extremely soluble in water, the liquid will rush up into the tube and completely fill it, showing that no free hydrogen or chlorine remains in the tube.

(2.) For all ordinary purposes, hydrochloric acid is always obtained by the action of sulphuric acid upon sodium chloride. For laboratory uses the apparatus seen in Fig. 94 may be conveniently employed. Sulphuric acid, previously diluted with rather less than its own volume of water, is placed in the flask, and a quantity of common salt is added. On the application of a gentle heat a steady stream of gas is evolved, which may be dried by being passed through the tubulated bottle, containing pumice moistened with strong sulphuric acid. The gas is then collected either over mercury, or by displacement. The reaction which takes place is expressed by the equation—

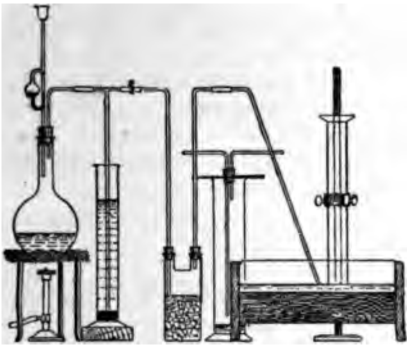


FIG. 94.

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

If strong sulphuric acid be employed along with an excess of salt, both of the atoms of hydrogen can be displaced from the acid; and instead of the hydrogen sodium sulphate, there is formed the normal sodium sulphate—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

A much higher temperature is necessary in order to complete the reaction indicated by this equation.

**Properties.**—Hydrochloric acid is a colourless gas with a choking, pungent odour. In contact with the moist air it forms dense fumes, consisting of minute globules of a solution of the gas in the atmospheric aqueous vapour. Hydrochloric acid does not burn, neither does it support ordinary combustion.

It is heavier than air, its specific gravity being—

$$\frac{18.185}{14.44} = 1.25 \text{ (air} = 1\text{)}.$$

Hence the gas is readily collected by displacement. One litre of the gas weighs 18.185 criths.

Hydrochloric acid is extremely soluble in water; 1 volume of water at 0° and under a pressure of 760 mm. is capable of dissolving 503 volumes of gaseous hydrochloric acid, measured at 0° and 760 mm. As the temperature rises the solubility diminishes, as seen by the following table:—

| Temperature. | Coefficient of Absorption. |
|---|---|
| 0° | 503 |
| 30° | 411 |
| 50° | 364 |

The solubility of hydrochloric acid may be illustrated by completely filling a large globular flask with the gas, by displacement, the flask being provided with a long tube passing through the cork, as seen in Fig. 95. On opening this tube beneath water, the gas begins to dissolve, and the liquid rises slowly in the tube until it reaches the top. As soon as the first few drops enter the globe, they rapidly absorb the gas, thereby causing a partial vacuum in the vessel, so that the water is driven up the tube with considerable force, forming a fountain, which continues until the globe is nearly filled with liquid. If the water in the dish is rendered blue by the addition of litmus solution, the acid nature of the solution of the gas will be evident by the reddening of the liquid as it enters the globe.

When a weak aqueous solution of hydrochloric acid is boiled, it loses water and becomes stronger; while, on the other hand, if a strong solution be heated, it loses gas and becomes weaker, until in both cases an acid containing 20.24 per cent. of HCl is produced which boils at 110°. This strength of acid corresponds to a composition expressed by the formula $HCl + 8H_2O$, and it was at one time supposed to represent a definite compound. Roscoe and Dittmar have shown, however, that, as with nitric acid, the composition of the liquid which boils at a constant temperature is simply a function of the pressure.

The strongest aqueous solution of hydrochloric acid at 15° C. has a specific gravity of 1.212, and contains 42.9 per cent. of HCl.

Hydrochloric acid gas is readily liquefied by pressure. At a temperature of 10° a pressure of 40 atmospheres will effect its liquefaction. If the temperature be lowered to −16°, the same result is obtained by a pressure of 20 atmospheres. The critical temperature of hydrochloric acid is 52.3°.

Condensed hydrochloric acid is a colourless liquid. Gore has shown that this liquefied acid is without action on most of the metals which are readily dissolved by the aqueous acid.

The composition of hydrochloric acid may be experimentally proved by a number of methods. It may be shown synthetically by the volumetric experiment referred to above (page 326).

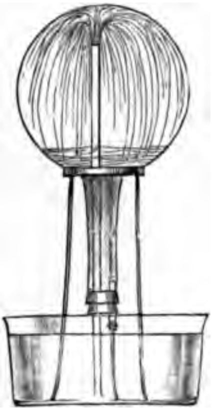


FIG. 95.

The volumetric proportion of hydrogen contained in the gas may be shown by means of sodium amalgam. The sodium in the amalgam, acts upon the hydrochloric acid, combining with the chlorine, and liberating the hydrogen—

$$Na + HCl = NaCl + H.$$

For this purpose gaseous hydrochloric acid is introduced into one limb of the U-shaped eudiometer (Fig. 96), and its volume indicated by means of a ring upon the tube, the mercury being level in both limbs. A second ring marks exactly half the volume. A quantity of liquid sodium amalgam is then poured into the open limb until it is completely filled, and on being closed by the thumb the tube can be inverted so as to decant the gas into this limb. After being bubbled once or twice through the amalgam, the gas is again returned *to its former place*; and by drawing mercury from the branch tube, the levels in each limb can be again adjusted, when it will be found that the gas remaining in the tube occupies the space exactly down to the upper ring, that is to say, two volumes of hydrochloric acid contain one volume of hydrogen. That the gas is hydrogen can be shown by again filling up the open limb with mercury, and driving the gas out of the stop-cock, where it can be inflamed as it escapes.

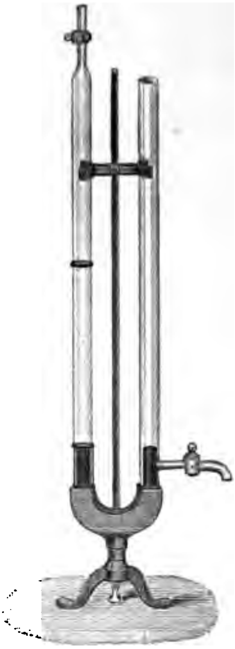


FIG. 96.

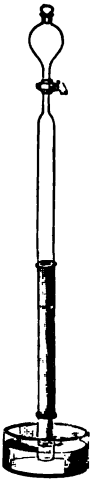


FIG. 97.

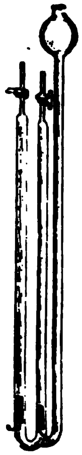


FIG. 98.

The fact that hydrochloric acid contains the same volume of chlorine as of hydrogen, may also be demonstrated by collecting the mixed gases, evolved by the electrolysis of the aqueous acid, in a long tube provided with a stoppered funnel, as shown in Fig. 97. The gases may be collected over a saturated solution of salt in water, and the tube filled to the lower ring. On allowing a solution of potassium iodide to enter by means of the funnel, the chlorine is absorbed with the liberation of iodine, which partially dissolves and partly separates as a solid. When the absorption of the chlorine is complete, the water will have risen to the second band placed half way up the tube, showing that one-half of the gaseous mixture consists of chlorine. The former experiment proved that hydrochloric acid contained half its volume of hydrogen, therefore the two elements, in uniting to form this compound, do so in equal volumes and without any contraction in volume.

When aqueous hydrochloric acid is subjected to electrolysis, the hydrochloric acid is decomposed, hydrogen being evolved at the negative electrode and chlorine at the positive. At first the liberated chlorine is dissolved in the solution ; but after the liquid has become saturated with the gas, the whole of the chlorine is liberated. By conducting this decomposition in the apparatus seen in Fig. 98, and continuing the passage of the electric current until the liquid in one limb is saturated with chlorine before closing the stop-cocks, it will be seen, when the gases are collected in the tubes, that they are evolved in equal volumes.

**The Manufacture of Hydrochloric Acid.**—The aqueous solution of hydrochloric acid is an object of commercial manufacture, which is carried out on an enormous scale. It is obtained by the decomposition of common salt by means of sulphuric acid, according to the reaction—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

Formerly hydrochloric acid was a waste product obtained in the manufacture of sodium carbonate by the method known as the *Leblanc process ;* the first stage in this process being the conversion of sodium chloride into sodium sulphate, by the action upon it of sulphuric acid. The hydrochloric acid evolved as gas in this reaction was allowed to escape into the atmosphere. The nuisance caused by this acid gas being thrown into the air, ultimately resulted in the "Alkali Act," which compelled manufacturers to absorb this waste acid. Since that time, the Leblanc process for the manufacture of sodium carbonate has had a formidable rival in another method, known as the *ammonia-soda process* (see Sodium Compounds), which would probably have completely driven the older method out of the field, but for the commercial value of the hydrochloric acid which is obtained as a secondary product in the Leblanc process. The hydrochloric acid, therefore, which formerly was thrown away as a waste product, is now the salvation of the process, and the utmost care is taken to prevent any of it from escaping, not now by compulsion of the Alkali Act, so much as from purely economic reasons.

The charge of salt and sulphuric acid is heated in an enormous *hemispherical cast-iron pan,* built into a brickwork chamber, so that it can be heated by a fire beneath, and so that the evolved gas can be conveyed away by brick or earthenware flues. The gas evolved by the reaction, is led into towers which are filled with coke or bricks, and down which water is made to percolate; the water being caused to flow equally over the mass, by means of special distributing contrivances. As the gaseous hydrochloric acid passes up the towers and meets the descending stream of water, it is entirely dissolved, and the aqueous acid becomes nearly saturated as it reaches the bottom of the tower.

In works where the condensers, or towers, are not of great height, it is usual either to cool the gas before admitting it into the towers, or to pass it through a series of jars, resembling gigantic Woulf's bottles (Fig. 99).

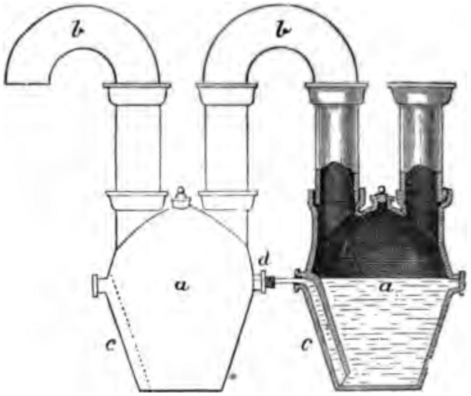


FIG. 99.

The water in these bottles is made to flow steadily from one to the other by the side pipes *c*, *c* (in the direction from left to right), while the gas passes through the system in the opposite direction. In this way a constantly changing surface of water is exposed to the gas, and a very strong solution is obtained.

Commercial hydrochloric acid is generally yellow in colour, owing to the presence of iron as an impurity; and it is always liable to contain sulphuric acid, free chlorine, arsenic, and sometimes sulphur dioxide. This aqueous solution of hydrochloric acid is also known under the names of "spirits of salt," and *muriatic* acid.

## *OXIDES AND OXYACIDS OF CHLORINE.*

The elements oxygen and chlorine have never been made to unite together directly: two compounds, however, of these elements can be obtained by indirect methods; these are—

| | |
|---|---|
| Chlorine monoxide (hypochlorous anhydride) | $Cl_2O$. |
| Chlorine peroxide | $ClO_2$. |

Three oxyacids are known, viz.:—

| | |
|---|---|
| Hypochlorous acid | $HClO$. |
| Chloric acid | $HClO_3$. |
| Perchloric acid | $HClO_4$. |

### CHLORINE MONOXIDE (*Hypochlorous anhydride*).

Formula, $Cl_2O$. Molecular weight = 86.70. Density = 43.35.

**Mode of Formation.**—This compound is obtained by passing dry chlorine over dry precipitated mercuric oxide contained in a glass tube, the temperature of which is not allowed to rise. The chlorine combines with the mercuric oxide, forming mercuric oxychloride, and chlorine monoxide is liberated—

$$2HgO + 2Cl_2 = HgO,HgCl_2 + Cl_2O.$$

**Properties.**—At ordinary temperatures chlorine monoxide is a pale yellow gas, without the greenish tint possessed by chlorine. Its smell strongly suggests chlorine, but is readily distinguishable from it. It is a very unstable compound, decomposing with more or less violence with moderate rise of temperature. When strongly cooled it is condensed to an orange-yellow coloured liquid, which boils at about $-20°$. This liquid is extremely unstable, exploding with great violence on the gentlest application of heat, and sometimes on merely being poured from one vessel to another. When exposed to direct sunlight it also explodes with violence.

Gaseous chlorine monoxide is considerably soluble in water, one volume dissolving about 100 volumes of the gas, forming hypochlorous acid—

$$Cl_2O + H_2O = 2HClO.$$

### CHLORINE PEROXIDE.

Formula, $ClO_2$. Molecular weight = 67.29. Density = 33.645.

**Modes of Formation.**—(1.) By the action of sulphuric acid upon potassium chlorate—

$$3KClO_3 + 2H_2SO_4 = KClO_4 + 2HKSO_4 + H_2O + 2ClO_2$$

Finely powdered potassium chlorate is added little by little to concentrated sulphuric acid in a small retort. The salt dissolves with the formation of a reddish liquid, and if the temperature is not allowed to rise, no gas is evolved. On very cautiously warming the retort by means of warm water, taking care not to heat the glass above the level of the liquid in the retort, the chlorine peroxide is evolved.

(2.) A mixture of chlorine peroxide and carbon dioxide, in equa volumes, is obtained by heating a mixture of powdered potassiu chlorate and oxalic acid to a temperature of 70° in a water-bath—

$$2KClO_3 + 2H_2C_2O_4 = K_2C_2O_4 + 2H_2O + 2CO_2 + 2ClO_2$$

(3.) Chlorine peroxide, mixed with chlorine, is evolved by t action of hydrochloric acid upon potassium chlorate—

$$4KClO_3 + 12HCl = 4KCl + 6H_2O + 9Cl + 3ClO_2$$

This mixture of gases was formerly supposed to be a defini compound of oxygen and chlorine, and received the name *euchlorine*.

**Properties.**—Chlorine peroxide is a heavy gas, with a de yellow colour. It has an intensely unpleasant smell, and if i haled, even when largely diluted with air, produces headac The gas attacks mercury, and is soluble in water, so that it c only be collected by displacement. Chlorine peroxide is an tremely unstable compound, it is gradually resolved into its e ments by the influence of light: the passage of an electric spa or the introduction into it of a hot wire, causes it to decomp with violent explosion. It is a powerful oxidising compound; piece of phosphorus introduced into the gas takes fire sponta ously. If a jet of sulphuretted hydrogen be lowered into a jar ne peroxide, the sulphuretted hydrogen ignites spontaneously, ontinues burning in the gas.

oxidising action upon organic matter, may be shown by ting the gas in the presence of such a substance as sugar, ding a drop of sulphuric acid to a mixture of powdered sugar otassium chlorate. The chlorine peroxide, liberated by the of the acid upon the chlorate, ignites the mixture, and the mass then bursts into flame.

en chlorine peroxide is strongly cooled, it condenses to dark uid, which is even more explosive than the gas.

## HYPOCHLOROUS ACID.

Formula, $HClO$.

**les of Formation.**—(1.) As already mentioned, this acid is d when chlorine monoxide is dissolved in water.

It may readily be obtained in dilute solution, by passing an of chlorine through water in which precipitated mercuric is suspended—

$$HgO + H_2O + 2Cl_2 = HgCl_2 + 2HClO.$$

distilling the liquid, the dilute acid passes over as a colourless ite.

In dilute solution, hypochlorous acid may be obtained by the position of a hypochlorite by a very dilute mineral acid, and uent distillation of the mixture; thus, if to a solution of n hypochlorite (obtained by treating bleaching-powder with and filtering the solution) very dilute nitric acid be added e solution distilled, a dilute colourless acid is obtained—

$$Ca(ClO)_2 + 2HNO_3 = Ca(NO_3)_2 + 2HClO.$$

This compound is also formed, when a stream of chlorine is l through water containing precipitated calcium carbonate in sion—

$$CaCO_3 + H_2O + 2Cl_2 = CaCl_2 + CO_2 + 2HClO.$$

**perties.**—Pure hypochlorous acid, free from water, has been obtained. The acid produced by the solution in water orine monoxide, has a pale straw-yellow colour, and a very characteristic chlorous smell. Dilute solutions of this acid moderately stable, while more concentrated solutions rea undergo spontaneous decomposition.

Hypochlorous acid is a powerful oxidising and bleaching ag as it readily gives up its oxygen, and is resolved into hydrochlo acid—

$$HClO = HCl + O.$$

As an oxidising agent it is twice as effective as an equivale quantity of chlorine in chlorine water, for two atoms of chlorine here necessary for the liberation of one atom of oxygen—

$$Cl_2 + H_2O = 2HCl + O.$$

Hypochlorous acid is decomposed by hydrochloric acid, wi the evolution of chlorine—

$$HClO + HCl = H_2O + Cl_2.$$

It is also decomposed by silver oxide, oxygen being liberated—

$$Ag_2O + 2HClO = 2AgCl + H_2O + O_2.$$

The salts of hypochlorous acid may be obtained by the action of the acid upon the hydroxides of the metals; thus—

$$HClO + KHO = KClO + H_2O.$$

The most important salt of this acid is *bleaching-powder* (see Calcium Salts).

## CHLORIC ACID.

Formula, $HClO_3$.

**Mode of Formation.**—This compound is best obtained, by decomposing barium chlorate with an exact equivalent of sulphuric acid, previously diluted with water—

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3.$$

The clear liquid is decanted from the precipitated barium sulphate, and is then concentrated by evaporation in vacuo.

The strongest acid that can be obtained still contains 80 per cent. of water. Attempts to concentrate it further, result in its decomposition into free chlorine and oxygen, with the formation of perchloric acid and water.

**Properties.**—The strong aqueous acid has powerful oxidising properties; many organic substances, as wood or paper, are so rapidly oxidised by it that when the acid is dropped upon them they are frequently inflamed.

The acid even in dilute solution has strong bleaching powers.

The salts of chloric acid are far more stable than the acid, and some of them are of considerable technical importance. The chlorates are all soluble in water, and all yield oxygen on being heated. Chloric acid is a monobasic acid; the chlorates, therefore, have the general formula $M'ClO_3$ and $M''(ClO_3)_2$, where M′ and M″ stand for monovalent and divalent metals respectively.

Of all the chlorates, potassium chlorate, $KClO_3$, is by far the most important. (See Potassium Compounds.)

## PERCHLORIC ACID.

Formula, $HClO_4$.

**Mode of Formation.**—Perchloric acid is best prepared, by the action of strong sulphuric acid upon potassium perchlorate—

$$2KClO_4 + H_2SO_4 = K_2SO_4 + 2HClO_4.$$

Pure and dry potassium perchlorate is mixed with four times its weight of concentrated sulphuric acid, and the mixture gently distilled in a small retort. The distillate at first consists of perchloric acid; but as the operation proceeds, a portion of the perchloric acid is decomposed into lower oxides of chlorine, and water, and the latter, combining with the first portions of the distillate, forms a white crystalline compound, having the composition $HClO_4,H_2O$. This body, when gently heated, gives off perchloric acid; it may, therefore, be employed for the preparation of the acid in a state of purity.

**Properties.**—Perchloric acid is a colourless, volatile, and strongly fuming liquid, having a specific gravity of 1.782 at 15°. It is an extremely powerful oxidising substance; a drop of the liquid allowed to fall upon paper, wood, or charcoal is instantly decomposed, sometimes with a violent explosion. In contact with the skin it produces most painful wounds ; when allowed to drop into water it produces a hissing sound, owing to the energy of the combination.

Perchloric acid cannot be preserved, as it slowly decomposes even in the dark, and often explodes spontaneously.

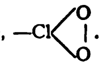
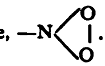
The salts of this acid are the perchlorates, of which the most important is potassium perchlorate ; they are all soluble in water.

**Constitution of the Oxides and Oxyacids of Chlorine.**—On the assumption that chlorine is a monovalent element, the constitution of these compounds may be thus represented :—

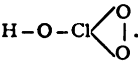
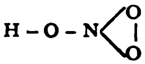
Chlorine monoxide, $\mathrm{Cl-O-Cl}$. | Hypochlorous acid, $\mathrm{Cl-O-H}$.
Chlorine peroxide, $\mathrm{Cl-O-O-}$. | Chloric acid, $\mathrm{Cl-O-O-O-H}$.
Perchloric acid, $\mathrm{Cl-O-O-O-O-H}$.

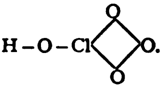
It is possible, however, that in some of these compounds the chlorine functions as a trivalent element, and that these compounds have a constitution similar to the oxides and oxyacids of nitrogen, thus—

Chlorine monoxide, $\mathrm{Cl-O-Cl}$. Nitrogen monoxide, $\mathrm{N-O-N}$.

Chlorine peroxide,  $-\mathrm{Cl}\left\langle\begin{matrix}\mathrm{O}\\ |\\ \mathrm{O}\end{matrix}\right.$. Nitrogen peroxide,  $-\mathrm{N}\left\langle\begin{matrix}\mathrm{O}\\ |\\ \mathrm{O}\end{matrix}\right.$.

Hypochlorous acid, $\mathrm{Cl-O-H}$. Hyponitrous acid, $\mathrm{N-O-H}$.

Chloric acid,  $\mathrm{H-O-Cl}\left\langle\begin{matrix}\mathrm{O}\\ |\\ \mathrm{O}\end{matrix}\right.$. Nitric acid,  $\mathrm{H-O-N}\left\langle\begin{matrix}\mathrm{O}\\ |\\ \mathrm{O}\end{matrix}\right.$.

Perchloric acid,  $\mathrm{H-O-Cl}\left\langle\begin{matrix}\mathrm{O}\\ \\ \mathrm{O}\end{matrix}\right\rangle\mathrm{O}$.

There are several facts which point to the belief that not only chlorine, but also bromine and iodine, are capable of fulfilling the functions of a trivalent element. The existence, for example, of such a compound as trichloride of iodine, $ICl_3$, is difficult to explain on any other assumption than that iodine is here a trivalent element.

Indeed, from a consideration of the salts of periodic acid, some chemists are in favour of assigning to iodine even a still higher valency, and of regarding it as a heptad element in these compounds (see Periodates, page 356). The constitution of such molecules as those of hydrofluoric acid at low temperatures, namely, $H_2F_2$, and of the acid fluoride of potassium, HF,KF, is readily understood if we regard the fluorine as functioning in these compounds as a trivalent element, thus—

$$\mathrm{H-F=F-H}, \text{ and } \mathrm{H-F=F-K}.$$

## BROMINE.

Symbol, Br. Atomic weight = 79.76. Molecular weight = 159.52.
Vapour density = 79.76.

**History.**—This element was discovered by Balard (1826), in the mother-liquor obtained after the crystallisation of salt from concentrated sea-water. He applied the name *bromine* (signifying a *stench*) to the element, in allusion to its unpleasant smell.

**Occurrence.**—Bromine is never found in the uncombined state in nature. In combination chiefly with the metals potassium, sodium, and magnesium, it occurs in small quantities in all sea-water, and more abundantly in many mineral waters and salt springs. The saline deposits of Stassfurt contain notable quantities of bromides, and the main supply of bromine for the market is manufactured from this source.

**Modes of Formation.**—(1.) Bromine may be obtained from a bromide by displacement with chlorine. If to a solution of magnesium bromide, chlorine water is added, the chlorine combines with the magnesium and the bromine is liberated—

$$MgBr_2 + Cl_2 = MgCl_2 + Br_2.$$

On distilling the liquid the bromine is driven off, and can be collected in a well-cooled receiver. The addition of any excess of chlorine results in the formation of bromide of chlorine, and is therefore to be avoided.

(2.) Bromine is readily obtained from potassium bromide by the action of manganese dioxide and sulphuric acid, a reaction exactly analogous to that by which chlorine is obtained from sodium chloride—

$$2KBr + MnO_2 + 2H_2SO_4 = MnSO_4 + K_2SO_4 + 2H_2O + Br_2.$$

The mixture is gently distilled from a retort into a receiver kept cold by means of ice.

(3.) **Manufacturing Methods.**—Practically all the bromine that is required at the present day, is manufactured from crude carnallite obtained at Stassfurt (see Alkali Metals). This salt contains bromine combined with magnesium, the magnesium bromide forming about 1 per cent. of the magnesium chloride in the crude substance. The final mother liquors from the manufacture of potassium chloride, and which were formerly run to waste, are found to contain about .25 per cent. of bromine as magnesium bromide, and these liquors are now utilised for the manufacture of bromine.

The bromine is liberated from its combination with magnesium, by means of chlorine. In some processes, the mother liquor is mixed with manganese dioxide and sulphuric acid in a stone vessel resembling an ordinary chlorine still. The magnesium chloride in the liquor, is acted upon by the manganese dioxide and sulphuric acid with the evolution of chlorine, and this decomposes the bromide present, displacing the bromine—

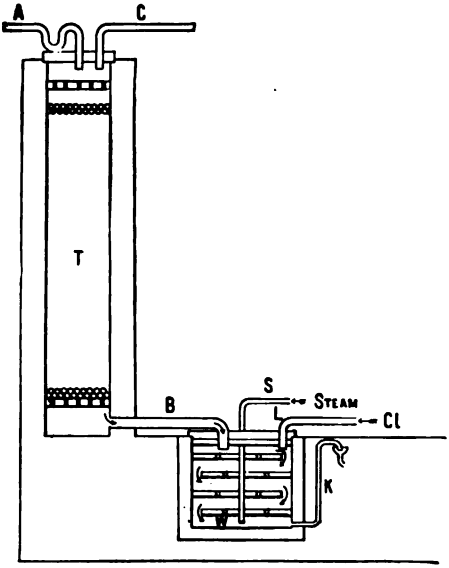


Fig. 100.

$$MgCl_2 + MnO_2 + 2H_2SO_4 = MnSO_4 + MgSO_4 + 2H_2O + Cl_2.$$
$$MgBr_2 + Cl_2 = MgCl_2 + Br_2.$$

The bromine that is driven out, is condensed by means of a worm condenser.

Instead of the chlorine being generated within the mother liquor, it is now more usually produced in a separate chlorine still, and passed into the liquor. Fig. 100 shows in diagrammatic form the method employed. The hot mother liquor is admitted by the pipe A into the tower T, which is filled with earthenware balls, between which the liquid percolates. It leaves the tower by the pipe B, and flows into the tank W, which is provided with shelves in such a way that the liquid must circulate through it in the direction indicated by the arrows. The exit-pipe from this tank, empties into a waste, placed at such a height that the tank is always nearly full. The liquid in the tank is kept at, or near, the boiling-point, by means of a current of steam blown in through S. Chlorine from a still is admitted by the pipe L, and passing into the tower by the pipe B, travels in an opposite direction to the current of liquid. As the chlorine passes up the tower, it meets the descending mother liquor, and decomposes the magnesium bromide contained in it with the liberation of bromine. The bromine vapour leaves the tower by the pipe C, and is conveyed to a worm (Fig. 101), where it is condensed. Any bromine which dissolves in the water in the tower, is again expelled from solution by the steam as the liquid traverses the tank W, and is swept up into the tower by the current of chlorine. The condensed bromine, as it leaves the worm, is collected in a tubulated *bottle, and any* vapour which escapes condensation

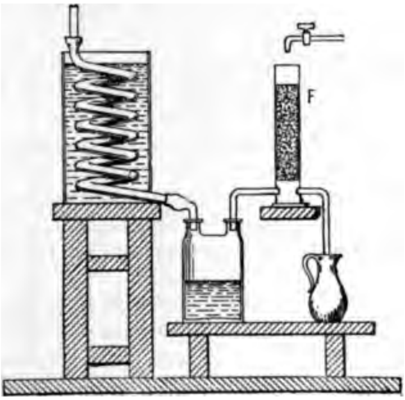


FIG. 101.

is arrested by the vessel F, Fig. 101. This tube is filled with iron borings, kept moist by the constant dropping of water upon them, and any bromine, or bromide of chlorine, is there converted into iron compounds, which are dissolved by the water, and flow away into the receiver. The bromine is purified by redistillation.

**Properties.**—Bromine is a heavy but mobile liquid, of a deep reddish-brown colour. Except in extremely thin layers it is opaque. It is the only non-metallic element which is liquid at the ordinary temperature. Bromine boils at 59°, but being a very volatile liquid it gives off vapour rapidly at the ordinary temperature. A drop of bromine allowed to fall into a flask, immediately evaporates and fills the vessel with a dark red-brown vapour. The specific gravity of the liquid at 0° is 3.188. At $-7°$ bromine solidifies to a crystalline mass. Bromine has a powerful and disagreeable smell. When the vapour, largely diluted with air, is inhaled, it suggests chlorine by its smell and by its action upon the mucous membrane of the throat and nose; it has in addition, however, a most irritating action upon the eyes. It is very poisonous, and the liquid exerts a corrosive action upon the skin; it produces a yellow colour when brought in contact with starch.

The vapour density of bromine, taken at moderately high temperatures, gradually becomes less than is demanded by the formula $Br_2$, showing that dissociation takes place. In the case of bromine this is more marked than with chlorine.

Bromine is soluble in water, imparting its own colour to the solution which is known as *bromine water*. 100 grammes of water at 0° dissolve 3.60 grammes of bromine. The solubility steadily diminishes as the temperature rises: at 20° it is 3.208, and at 30° it is 3.126.

When bromine water is cooled to 0° it deposits a crystalline hydrate similar in composition to the hydrate of chlorine, $Br_2,10H_2O$.

Bromine resembles chlorine in its chemical attributes; it combines directly with metals and many other elements, although with less energy than is exhibited by chlorine. A fragment of arsenic, for example, when dropped upon bromine, ignites and burns upon the surface of the liquid.

Like chlorine, it has bleaching properties, due to its power of combining with hydrogen.

## HYDROBROMIC ACID.

Formula, HBr. Molecular weight = 80.76. Density = 40.38.

**Modes of Formation.**—(1.) Hydrobromic acid can be obtained by the direct union of its elements. Bromine vapour and hydrogen, when mixed, do not combine under the influence of light; neither does such a mixture explode when a light is applied to it. The mixture, however, may be caused to burn, when hydrobromic acid is formed; or, if the mixed gases be passed through a red-hot tube, the same result follows. A simple method of preparing hydrobromic acid synthetically, consists in passing a mixture of hydrogen and bromine vapour over a spiral of platinum wire, maintained at a red heat by means of an electric current.*

(2.) The best method for the preparation of gaseous hydrobromic acid, consists in dropping bromine upon red phosphorus which has been moistened with a small quantity of water, when tribasic phosphoric acid is formed, and hydrobromic acid is liberated—

$$P + 4H_2O + 5Br = H_3PO_4 + 5HBr.$$

We may suppose that in this reaction the bromides of phosphorus are formed and simultaneously decomposed, the action of water upon these compounds being thus expressed—

$$PBr_3 + 3H_2O = H_3PO_3 + 3HBr.$$
$$PBr_5 + 4H_2O = H_3PO_4 + 5HBr.$$

(3.) Hydrobromic acid may be obtained by the action of phosphoric acid upon potassium bromide—

$$3KBr + H_3PO_4 = K_3PO_4 + 3HBr.$$

(4.) If sulphuric acid be employed (as in the formation of hydrochloric acid from a chloride), free bromine is simultaneously produced, owing to the reduction of a portion of the sulphuric acid by the hydrobromic acid which is first evolved, thus—

$$H_2SO_4 + 2HBr = SO_2 + 2H_2O + Br_2.$$

(5.) A dilute aqueous solution of hydrobromic acid may also be obtained by passing a stream of sulphuretted hydrogen through bromine water—

---

* See "Chemical Lecture Experiments," No. 218.

$$SH_2 + Br_2 = S + 2HBr.$$

(6.) Hydrobromic acid is readily obtained, by the action of bromine upon certain hydrocarbons, such as turpentine or melted paraffin. The action is one of substitution, one atom of bromine replacing one atom of hydrogen in the compound, and the hydrogen so displaced combining with a second bromine atom to form hydrobromic acid. Thus, if the hydrocarbon be represented by the general formula, $C_nH_{2n+2}$, the action of bromine will be represented thus—

$$C_nH_{2n+2} + Br_2 = C_nH_{2n+1}Br + HBr.$$

**Properties.**—Hydrobromic acid is a colourless, pungent-smelling gas, which fumes strongly in the air. It is extremely soluble in water, forming an acid liquid strongly resembling aqueous hydrochloric acid.

When boiled, this solution loses either acid or water, until it reaches a degree of concentration at which it contains 48 per cent. of hydrobromic acid. The acid of this strength then continues to boil unchanged at 126°. As with hydrochloric acid, the strength of the liquid which boils at a constant temperature, depends upon the pressure.

Hydrobromic acid is decomposed by chlorine, with the liberation of bromine—

$$2HBr + Cl_2 = 2HCl + Br_2.$$

In its chemical behaviour, hydrobromic acid closely resembles hydrochloric acid, and this resemblance is extended to the bromides. All bromides are soluble in water, except mercurous bromide, silver bromide, and lead bromide, the latter being slightly soluble.

## *OXYACIDS OF BROMINE.*

No oxides of bromine corresponding with the oxides of chlorine have as yet been obtained; two oxyacids, however, are known, viz.—

| | |
|---|---|
| Hypobromous acid . . . . | $HBrO$. |
| Bromic acid . . . . . | $HBrO_3$. |

## HYPOBROMOUS ACID.

Formula, HBrO.

**Mode of Formation.**—An aqueous solution of hypobromous acid may be obtained, by shaking together a mixture of bromine water and precipitated mercuric oxide, the reaction being analogous to that by which hypochlorous acid is prepared—

$$HgO + H_2O + 2Br_2 = HgBr_2 + 2HBrO.$$

**Properties.**—Hypobromous acid is an unstable compound; it breaks up on distillation into oxygen and bromine. By heating to 40° in vacuo, however, it can be distilled without decomposition. The aqueous liquid so obtained has a pale yellow colour. It readily gives up its oxygen, and is a strong bleaching agent; when heated to about 60° it decomposes.

## BROMIC ACID.

Formula, $HBrO_3$.

**Modes of Formation.**—(1.) This acid is only known in aqueous solution; in this form it may be obtained by the action of bromine upon silver bromate in the presence of water—

$$5AgBrO_3 + 3Br_2 + 3H_2O = 5AgBr + 6HBrO_3.$$

The insoluble silver bromide separates out, and the aqueous acid can be decanted from the precipitate.

(2.) A solution of this acid, mixed with hydrochloric acid, is also formed when chlorine is passed through bromine water—

$$Br_2 + 5Cl_2 + 6H_2O = 10HCl + 2HBrO_3.$$

(3.) The decomposition of barium bromate by the requisite weight of sulphuric acid, affords the best method for the preparation of a pure aqueous solution of bromic acid—

$$Ba(BrO_3)_2 + H_2SO_4 = BaSO_4 + 2HBrO_3.$$

**Properties.**—Bromic acid is an unstable, strongly acid substance, closely resembling chloric acid. The aqueous solution may be concentrated *in vacuo* until it contains about 50 per cent.

of bromic acid, representing a composition of 1 molecule of the acid to 7 of water. Beyond this degree of concentration, or if heated to 100°, the acid decomposes into bromine, oxygen, and water.

The bromates are formed by reactions similar to those by which the chlorates are produced; thus, by adding bromine to a solution of potassium hydroxide, a mixture of potassium bromide and bromate is obtained—

$$6KHO + 3Br_2 = 5KBr + KBrO_3 + 3H_2O.$$

And the two salts can be separated by crystallisation, owing to the greater solubility of the bromide.

The bromates decompose on being heated, some with the liberation of oxygen and formation of bromide—

$$KBrO_3 = KBr + 3O,$$

but without the intermediate production of a perbromate. Others give off their bromine as well as a part of the oxygen they contain, leaving the metal in combination with oxygen—

$$Mg(BrO_3)_2 = MgO + Br_2 + 5O.$$

## IODINE.

Symbol, I. Atomic weight = 126.54. Molecular weight = 253.08.
Vapour density = 126.54.

**History.**—Iodine was discovered by Courtois (1812), who observed that a beautiful violet vapour was evolved, during his endeavours to prepare nitre from liquors obtained by lixiviating the ashes of burnt seaweed. The substance was subsequently investigated by Gay-Lussac.

**Occurrence.**—Like all the other members of this group of elements, iodine is never found in nature in the uncombined condition. In combination it occurs associated principally with potassium, sodium, magnesium, and calcium, as iodides and iodates.

Iodine is a widely distributed element, although not occurring in more than small quantities in any particular source. Thus it is found in small quantities in sea-water and in both marine plants and animals. The amount of iodine in seaweed varies with different plants ; generally speaking, those from greater depths, contain more than weeds which grow in comparatively shallow waters.

| | Dry Weeds. | Per Cent. of Iodine. |
|---|---|---|
| Drift weed | Laminaria digitata (stem) | 0.4535 |
| | Laminaria stenophylla | 0.4777 |
| Cut weed | Fucus serratus | 0.0856 |
| | Ascophyllum nodosum | 0.0572 |

Iodine is also found in small quantities in many mineral waters and medicinal springs.

In small quantities iodine is present in the natural sodium nitrate of Chili and Peru, known as Chili saltpetre, and at the present day this constitutes the most abundant source of this element.

**Mode of Formation.**—Iodine may be readily obtained by a precisely similar reaction to that by which both bromine and chlorine are produced ; thus, if potassium iodide be mixed with manganese dioxide and sulphuric acid, and the mixture gently heated in a retort, iodine distils over and condenses in the form of greyish black crystals—

$$2KI + MnO_2 + 2H_2SO_4 = K_2SO_4 + MnSO_4 + 2H_2O + I_2.$$

**Manufacturing Processes.**—On an industrial scale iodine is obtained from two sources, namely, from seaweed and from caliche (Chili saltpetre).

(1.) *From seaweed.* The weeds chiefly employed, are the *Laminaria digitata* and *Laminaria stenophylla.* The weed is burnt in shallow pits, care being taken to avoid too high a temperature ; the maximum yield of iodine being obtained if the ash is not allowed to fuse. This ash is technically known as *kelp*, and if the weed is properly burnt, it should yield a kelp containing from 25 to 30 lbs. of iodine per ton. The kelpers, however, usually lose about half the iodine on account of burning the weed at too high a temperature, thereby fusing the ash into a hard slag, instead of obtaining a porous residue.

An improved process of carbonising the weed, was introduced by Stanford (1863), in which it was heated in large retorts, whereby the volatile products of the distillation, consisting largely of tar and ammoniacal liquor, could be collected. The kelp obtained by this method is in a very porous condition, and contains the whole of the iodine originally present in the weed.

A still more recent process for extracting the iodine from seaweed, and at the same time obtaining other useful materials, has since been discovered by Stanford. The weed is boiled with sodium carbonate and filtered: the residue consists of a substance called *algulose*. Hydrochloric acid is added to the filtered liquid, which precipitates a compound known as *alginic acid*, and this is again separated by filtration. The liquor is neutralised with sodium hydrate, evaporated to dryness and carbonised. The residue, which is known as "kelp substitute," contains all the iodine, as well as the potash salts, and should yield about 30 lbs. of iodine per ton.

[The alginic acid obtained in this process, is purified and converted into the sodium salt, which constitutes the commercial "algin," a material of a gelatinous or albuminous nature which has lately been put to a number of useful applications.]

The kelp obtained by either of these methods, is lixiviated with water in large iron vats, whereby all the soluble salts are extracted. This aqueous liquid is concentrated in large open boiling pans, and the less soluble salts, viz., the alkaline sulphates, carbonates, and chlorides, are allowed to crystallise. The mother liquor is then mixed with sulphuric acid and allowed to stand. The sulphuric acid decomposes any sulphides and sulphites which may be present, with the separation of sulphur; it also converts the bromides and iodides into the corresponding sulphates, with the liberation of hydrobromic and hydriodic acids which remain in solution, while the alkaline sulphates are deposited from the liquid, and are technically known as *plate sulphate*. The liquor is then transferred to the *iodine still*, which is an iron pot furnished with a leaden cover into which two exit-pipes are fixed (Fig. 102). These are connected to a series (usually ten in each row) of large earthenware jars or *aludels*. A gentle heat is applied, and manganese dioxide is introduced from time to time through the opening. The iodine is evolved according to the following equation—

$$2HI + MnO_2 + H_2SO_4 = MnSO_4 + 2H_2O + I_2,$$

and condenses in the jars. These vessels are also furnished with a tubulus upon their under side, so that the water which is evolved during the distillation can drain out, and run off down the trough in which the jars are resting.

(2.) *From Chili saltpetre.* The crude sodium nitrate of Chili d Peru, known as *caliche*, contains small quantities of iodine, iefly as sodium iodate. Although the amount of iodine in iche is only very small, averaging about 0.2 per cent., in view f the enormous quantity of nitrate that is turned out, the aggre- te amount of iodine is very great. This iodine is now extracted, d the supply of this element that is now manufactured from this rce, is more than the total consumption of iodine in the whole rld. The process is based upon the fact, that when a solution

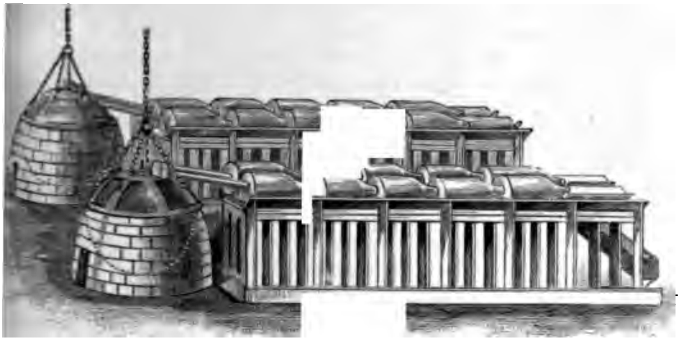


FIG. 102.

of hydrogen sodium sulphite (sodium bisulphite) is added to a solution of an iodate, iodine is precipitated, thus—

$$2NaIO_3 + 5NaHSO_3 = 3NaHSO_4 + 2Na_2SO_4 + H_2O + I_2.$$

The final mother liquor from the sodium nitrate, or caliche, in which all the iodate has concentrated, contains as much as 22 per cent. of this salt. This liquor is mixed with the requisite proportion of the hydrogen sodium sulphite solution, in large lead-lined vats, and the precipitated iodine allowed to settle. It is then washed and pressed into blocks, and is found to contain from 80 to 85 per cent. of iodine. This impure product is then distilled at a gentle heat from iron retorts, the vapour being condensed in a series of earthenware receivers much as in the older method.

**Properties.**—Iodine is a bluish-black shining solid, somewhat resembling graphite in lustre and general outward appearance. It crystallises in large brilliant plates, which have a specific gravity of 4.95. When heated to 107° iodine melts, and gives off vapour having a beautiful violet colour. Its boiling-point is about 175°.

Iodine vaporises slowly at ordinary temperatures, and sublimes from one part to another of a bottle in which a small quantity of it is contained. The smell of iodine vapour is somewhat irritating and unpleasant, recalling the smell of moderately diluted chlorine. When iodine vapour is heated, it passes from a violet colour to a deep indigo blue.* This change in the colour is accompanied by a diminution of the vapour density. Up to a temperature of 700° the density of iodine corresponds to the formula $I_2$: as the temperature is raised the density gradually diminishes, until at 1468 it is reduced to less than two-thirds. At this point, 73.1 per cent. of the iodine molecules have become dissociated into single atoms.

Iodine is slightly soluble in water, 1 gramme of iodine being dissolved by 5.524 litres of water at 10°. This dilute solution, however, has a perceptible brown colour. Iodine is freely soluble in aqueous potassium iodide solution, in alcohol, ether, and aqueous hydriodic acid; in all these solvents it dissolves to a dark reddish brown solution. In chloroform, carbon disulphide, and many liquid hydrocarbons, iodine is also soluble, but in these solvents it dissolves to a deep violet solution, resembling the colour of the vapour.

When iodine is brought in contact with starch, it forms an intense blue colour. This reaction is so extremely delicate, that it is capable of revealing the minutest trace of iodine. The exact nature of this blue compound is not known. The colour disappears when the liquid is heated to about 80°, but returns on cooling; continued boiling destroys it permanently.

In its chemical relations iodine resembles chlorine and bromine, but with a lesser degree of energy. Both these elements are capable of displacing iodine from its combinations with electro-positive elements, thus—

$$KI + Br = KBr + I.$$
$$KI + Cl = KCl + I.$$

Iodine combines with many elements, both metals and non-metals forming iodides. Phosphorus, when brought in contact with iodine, at once melts and inflames; antimony powder dropped into iodine vapour also spontaneously inflames. When mercury and iodine are gently heated, energetic combination takes place, and mercuric iodide is formed.

---

* "Chemical Lecture Experiments," No. 224.

### HYDRIODIC ACID.

Formula, HI. Molecular weight = 127.54. Density = 255.08.

**Modes of Formation.**—(1.) Hydriodic acid can be obtained synthetically, by passing a mixture of hydrogen and iodine vapour over strongly heated, finely divided platinum.

(2.) It is also obtained by the action of phosphoric acid upon sodium or potassium iodide—

$$3KI + H_3PO_4 = K_3PO_4 + 3HI.$$

As in the case of the corresponding bromine compound, sulphuric acid cannot be employed, as by its action upon the iodide, iodine and sulphur dioxide are liberated, thus—

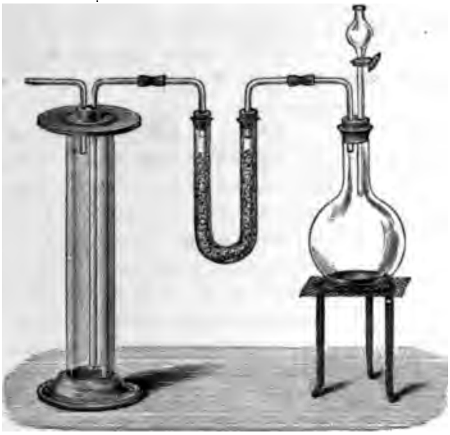


FIG. 103.

$$2KI + 3H_2SO_4 = 2HKSO_4 + 2H_2O + SO_2 + I_2.$$

(3.) Hydriodic acid is most readily prepared, by the action of phosphorus upon iodine in the presence of water—

$$P + 5I + 4H_2O = H_3PO_4 + 5HI.$$

The red phosphorus and iodine for this reaction may be placed in a dry flask, and water gradually dropped upon the mixture, when hydriodic acid is rapidly evolved. The gas is allowed to pass through a U-tube containing red phosphorus, in order to arrest any iodine vapour which may accompany it. Hydriodic acid may be collected over mercury or by displacement, as shown in Fig. 103.

**Properties.**—Hydriodic acid is a colourless, pungent-smelling gas, which fumes strongly on coming into the air. The gas is readily decomposed by heat into hydrogen and iodine. Thus, if a heated wire be thrust into the gas, or if a spiral of platinum wire be heated in the gas by means of an electric current, the violet vapour of iodine at once makes its appearance.

When mixed with chlorine, hydriodic acid is at once decomposed, with the liberation of iodine, thus—

$$2HI + Cl_2 = 2HCl + I_2.$$

Hydriodic acid is one of the most readily liquefied gases; at 0°, and under a pressure of four atmospheres, it condenses to a colourless liquid.

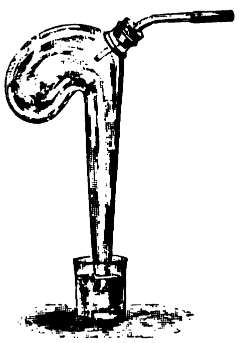


FIG. 104.

The gas is extremely soluble in water. An aqueous solution of it is readily produced, by allowing the gas, obtained by the method of preparation above described, to pass into water. In order to prevent the water from being drawn back into the generating flask, it is convenient to pass the gas through a retort arranged in the position seen in Fig. 104. Should there be any back rush of water, owing to the intermission of the evolution of gas in the apparatus, the liquid in the beaker will be drawn up into the retort and there lodge, leaving the end of the neck open to the air.

A saturated aqueous solution of hydriodic acid at 0° has a specific gravity of 2. At the ordinary pressure the strongest acid that can be obtained by distillation has a specific gravity of 1.67, and contains 57.7 per cent. of hydriodic acid. This solution boils at 127°. As in the case of the corresponding bromine and chlorine compounds, the particular strength of acid which has a constant boiling-point, is a function of the pressure.

Aqueous hydriodic acid, when freshly prepared, is colourless; but it rapidly turns brown, owing to the oxidation of the compound, and the solution of the liberated iodine in the acid—

$$4HI + O_2 = 2H_2O + 2I_2.$$

### *OXIDE AND OXYACIDS OF IODINE.*

One compound of iodine with oxygen is known, and two oxyacids, viz.:—

| | |
|---|---|
| Iodine pentoxide . . . . | $I_2O_5$. |
| Iodic acid . . . . . | $HIO_3$. |
| Periodic acid . . . . | $HIO_4$. |

### IODINE PENTOXIDE (*Iodic Anhydride*).

Formula, $I_2O_5$.

**Mode of Formation.**—When iodic acid is heated to 170°, it loses water and is converted into the pentoxide—

$$2HIO_3 = H_2O + I_2O_5.$$

**Properties.**—Iodine pentoxide is a white crystalline solid body. It is soluble in water, combining with a molecule of the water to form iodic acid. Iodine pentoxide is more stable than any of the oxides of the other halogens; but, when heated to a temperature of 300°, it decomposes into its elements.

### IODIC ACID.

Formula, $HIO_3$.

**Modes of Formation.**—(1.) Iodic acid can be prepared by adding to a solution of barium iodate the requisite amount of sulphuric acid demanded by the equation—

$$Ba(IO_3)_2 + H_2SO_4 = BaSO_4 + 2HIO_3.$$

The aqueous solution of iodic acid is decanted from the precipitated barium sulphate, and may be concentrated at 100° without being decomposed.

(2.) When chlorine is passed through water in which powdered iodine is suspended, a mixture of iodic acid and hydrochloric acid is produced—

$$3H_2O + I + 5Cl = 5HCl + HIO_3.$$

The hydrochloric acid may be removed by the addition of precipitated silver oxide to the solution, and separating the precipitated silver chloride by filtration.

(3.) Iodic acid is most conveniently prepared by heating iodine with nitric acid, whereby the iodine is oxidised, and a mixture of oxides of nitrogen is evolved as dense red vapours—

$$3HNO_3 + I = HIO_3 + H_2O + N_2O_3 + NO_2.$$

**Properties.**—Iodic acid is a white crystalline solid, soluble in water. The aqueous solution shows an acid reaction with litmus, but the colour is ultimately discharged by the bleaching action of the compound. Iodic acid does not form any blue colour with starch; being, however, an oxidising substance, it readily gives up oxygen to such reducing agents as sulphur dioxide, sulphuretted hydrogen, or hydriodic acid, with the liberation of iodine, thus—

$$2HIO_3 + 4H_2O + 5SO_2 = 5H_2SO_4 + I_2.$$
$$2HIO_3 + 5H_2S = 5S + 6H_2O + I_2.$$
$$HIO_3 + 5HI = 3H_2O + 3I_2.$$

If, therefore, a small quantity of sulphurous acid be added to a dilute solution of iodic acid, previously mixed with starch, the blue iodide of starch will be formed. This reaction affords an excellent illustration of the time required for certain chemical changes to go forward. It is readily possible to obtain an interval of 30 to 60 seconds between the addition of the sulphurous acid and appearance of any visible result, when at the expiration of that time the whole mass of the liquid suddenly turns blue.*

**Iodates.**—When iodine is dissolved in potassium hydroxide, a mixture of potassium iodide and iodate is produced, by an analogous reaction to that which takes place with either bromine or chlorine—

$$6KHO + 3I_2 = 5KI + KIO_3 + 3H_2O.$$

With the exception of the iodates of the alkali metals, the iodates are for the most part insoluble in water. On being heated they behave in a similar manner to the bromates, some being decomposed into an iodide and oxygen, while others leave a metallic oxide and evolve iodine as well as oxygen. The alkaline iodates are capable of uniting with iodic acid, forming salts which are termed *acid* and *di-acid* iodates, thus—

---

* See Experiment 237, "Chemical Lecture Experiments."

| | |
|---|---|
| Normal potassium iodate . . . | $KIO_3$. |
| Acid potassium iodate . . . | $KIO_3,HIO_3$. |
| Di-acid potassium iodate . . . | $KIO_3,2HIO_3$. |

## PERIODIC ACID.

Formula, $HIO_4,2H_2O$ or $H_5IO_6$.

**Modes of Formation.**—(1.) The compound represented by the formula $HIO_4$ has never been obtained; when aqueous solutions of periodic acid are evaporated, the compound which crystallises out has the composition $HIO_4,2H_2O$, or $H_5IO_6$.

It may be obtained by boiling silver periodate with water, when an insoluble basic silver salt is produced—

$$2AgIO_4 + 4H_2O = Ag_2H_3IO_6 + HIO_4,2H_2O.$$

The silver periodate is prepared by passing chlorine into an aqueous solution of sodium iodate and sodium hydroxide, when the sparingly soluble disodium periodate separates out—

$$NaIO_3 + 3NaHO + Cl_2 = 2NaCl + Na_2H_3IO_6.$$

This sodium salt is then dissolved in nitric acid, and silver nitrate added, whereby $AgIO_4$ is formed, which crystallises out on concentration—

$$\begin{cases} 2Na_2H_3IO_6 + 2HNO_3 = 2NaNO_3 + 4H_2O + 2NaIO_4. \\ 2NaIO_4 + 2AgNO_3 = 2NaNO_3 + 2AgIO_4. \end{cases}$$

(2.) Periodic acid is also formed by the addition of iodine to an aqueous solution of perchloric acid—

$$2HClO_4 + 2H_2O + I_2 = Cl_2 + 2HIO_4,2H_2O.$$

**Properties.**—The acid having the composition $HIO_4,2H_2O$ is a colourless, crystalline, deliquescent substance. It melts at 133°, and at 150° is decomposed into iodine pentoxide, water, and oxygen—

$$2H_5IO_6 = I_2O_5 + 5H_2O + O_2.$$

The acid cannot be converted into $HIO_4$ by heat, for oxygen is evolved as *soon as water begins* to be given off.

**The Periodates** constitute a numerous class of salts, many of them being of a highly complex composition. On the assumption that iodine is monovalent in these compounds, their classification is somewhat difficult, and they must be represented as associations of molecules of salts of the unknown mono-basic periodic acid, $HIO_4$, with metallic oxide and water in various proportions—thus, the silver periodate in the foregoing equation, $Ag_2H_3IO_6$, would be expressed by the formula, $2AgIO_4.Ag_2O.2H_2O$.

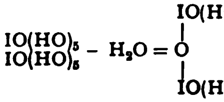
The classification of these compounds is much simplified, if we regard iodine as here functioning as a heptavalent element. On this assumption the periodates may be considered as the salts of various hypothetical acids, which are all derived from the compound $I(HO)_7$ (itself hypothetical) by the withdrawal of varying quantities of water. Thus, by the successive removal of one molecule of water the following three acids would be formed—

$I(HO)_7 - H_2O = IO(HO)_5$ . . . $H_5IO_6$. (1.)
$IO(HO)_5 - H_2O = IO_2(HO)_3$ . . . $H_3IO_5$. (2.)
$IO_2(HO)_3 - H_2O = IO_3(HO)$ . . . $HIO_4$. (3.)

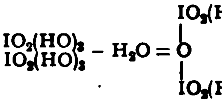
From these three acids the following salts may be regarded as being derived—

(1.) $Na_2H_3IO_6$; $Ag_2H_3IO_6$; $Ag_5IO_6$; $Ba_5(IO_6)_2$.
(2.) $Ag_3IO_5$; $Pb_3(IO_5)_2$.
(3.) $KIO_4$; $AgIO_4$.

By the abstraction of one molecule of water from *two* molecules of these acids, still more complex acids would be derived, thus—



$$\begin{matrix} IO(HO)_5 \\ IO(HO)_5 \end{matrix} - H_2O = \begin{matrix} IO(HO)_4 \\ | \\ O \\ | \\ IO(HO)_4 \end{matrix} \quad \text{or } H_8I_2O_{11}. \qquad (4.)$$



$$\begin{matrix} IO_2(HO)_3 \\ IO_2(HO)_3 \end{matrix} - H_2O = \begin{matrix} IO_2(HO)_2 \\ | \\ O \\ | \\ IO_2(HO)_2 \end{matrix} \quad \text{or } H_4I_2O_9. \qquad (5.)$$

And from these two acids the following periodates may be regarded as being derived—

(4.) $Zn_4I_2O_{11}$; $Ba_4I_2O_{11}$.
(5.) $Ag_4I_2O_9$; $Ca_2I_2O_9$; $Ba_2I_2O_9$.

## COMPOUNDS OF THE HALOGENS WITH EACH OTHER.

Chlorine unites both with bromine and with iodine, and the two latter elements combine with each other.

(1.) **Chlorine and Bromine.**—*Bromine monochloride.* This substance is obtained as a reddish-yellow liquid, when chlorine gas is passed into bromine. The compound is believed to have the composition BrCl.

(2.) **Chlorine and Iodine.**—*Iodine monochloride*, ICl. When dry chlorine is passed over iodine, the latter rapidly melts, forming a dark reddish-brown liquid, strongly resembling bromine in appearance. The liquid solidifies to a mass of red prismatic crystals, which melt at 25°. It is decomposed by water into iodic and hydrochloric acids, and iodine is liberated—

$$5ICl + 3H_2O = HIO_3 + 5HCl + 2I_2.$$

*Iodine trichloride*, $ICl_3$. This compound is formed by passing an excess of chlorine over iodine, or by passing chlorine through iodine monochloride. It is also formed when hydriodic acid is acted upon by an excess of chlorine—

$$HI + 2Cl_2 = HCl + ICl_3.$$

Iodine trichloride is a yellow solid substance, crystallising in long brilliant needle-shaped crystals, which sublime at the ordinary temperature. When gently warmed it melts, at the same time dissociating into chlorine and the monochloride; on cooling, re-union takes place with the reformation of $ICl_3$.

(3) **Bromine and Iodine.**—Two compounds of these elements are believed to exist, viz., a crystalline solid, and a deep-coloured liquid. Their composition is probably expressed by the formulæ, IBr and $IBr_3$.

# CHAPTER II

## THE ELEMENTS OF GROUP VI. (FAMILY B.)

| | | | |
|---|---|---|---|
| Oxygen, O | 15.96 | Selenium, Se | 78.87 |
| Sulphur, S | 31.98 | Tellurium, Te | 125 |

THE relation in which oxygen, the typical element, stands to the remaining members of the family is very similar to that between fluorine and the other halogens.

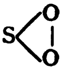
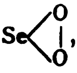
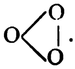
All the elements of this family unite with hydrogen, forming compounds of the type $RH_2$—

$$OH_2,\quad SH_2,\quad SeH_2,\quad TeH_2;$$

but the hydride of oxygen stands apart from the others in many of its attributes. Thus at ordinary temperatures it is a colourless and odourless liquid, while the remaining compounds are all fœtid-smelling and poisonous gases.

Sulphur, selenium, and tellurium each combine with oxygen, forming respectively $SO_3$, $SeO_3$, and $TeO_3$, while none of these elements in a divalent capacity forms a similar compound; that is to say, no such combinations are known as $OS_3$, or $OSe_3$, although amongst themselves they unite, forming $SeS_2$ and $TeS_2$.

Sulphur, selenium, and tellurium also unite with oxygen, forming dioxides, $SO_2$, $SeO_2$, and $TeO_2$, in which these elements are possibly tetravalent, in which case the constitution of the compounds will be represented thus, $O = S = O$; $O = Se = O$.

We may, however, consider them as functioning in a divalent capacity, and regard the oxides as constituted thus,  ; , in which case we may look upon ozone as being the corresponding oxygen compound, $OO_2$, .

All the elements of this family combine with chlorine, producing compounds having the following composition—

| Oxygen. | Sulphur. | Selenium. | Tellurium. |
|---|---|---|---|
| $O_2Cl$ | ... | ... | ... |
| ... | $S_2Cl_2$ | $Se_2Cl_2$ | ... |
| $OCl_2$ | $SCl_2$ | ... | $TeCl_2$ |
| ... | $SCl_4$ | $SeCl_4$ | $TeCl_4$ |

Oxygen again differs from the other members, by alone forming a compound of the type, $R_2Cl$. This element also shows no tendency to function with a higher atomicity than that of a divalent; while the others unite with four atoms of the halogen, thereby exhibiting their tetravalent nature.

The members of this family pass by a regular gradation from the strongly electro-negative, gaseous, non-metal oxygen, to the feebly negative and slightly basic element tellurium, which possesses many of the properties of a true metal. Selenium and tellurium are both elements which lie very close to that ill-defined boundary between the metals and non-metals, and are on this account sometimes termed *metalloids*. In tellurous oxide, $TeO_2$, we have a compound which is both an acid-forming and a salt-forming oxide, its acidic and basic properties being nearly equally balanced. Thus, it replaces hydrogen in sulphuric acid, forming tellurium sulphate, $Te(SO_4)_2$; and it also unites with water, forming tellurous acid, $H_2TeO_3$, corresponding to sulphurous acid, $H_2SO_3$.

Of the four elements of this family, oxygen is by far the most abundant, both in combination and in the free state; sulphur is more plentiful than the other two, and tellurium occurs in the smallest quantity.

The element oxygen has already been treated in Part II., p 159.

## SULPHUR.

Symbol, S. Atomic weight = 31.98. Molecular weight = 63.96.

**Occurrence.**—In the free state this element occurs chiefly in volcanic districts. In Italy and Sicily large quantities of *native sulphur* are found, which have long been the most important European sources of this substance. Large deposits are to be met with in Transylvania and in Iceland, and it also occurs in beds, often of great thickness, in parts of China, India, California, and the Yellowstone district of the Rocky Mountains. These natural deposits are sometimes found stratified with beds of clay or rock, but they often occur as what are known as "living" beds, in which the sulphur is continuously being formed as the result of chemical decompositions which are at present at work. Such a "living" sulphur bed is known as a *solfatara*, and, as in the case of the Iceland deposits, they are usually found associated with geysers, fumaroles, and other signs of volcanic action.

In combination with hydrogen, sulphur occurs as sulphuretted hydrogen. Enormous quantities of sulphur are found combined with various metals, constituting the important class of substances known as sulphides; as, for example, *galena*, or lead sulphide, PbS; *zinc blende*, or zinc sulphide, ZnS; *pyrites*, or iron sulphide, $FeS_2$; *copper pyrites*, or copper iron sulphide, $Cu_2Fe_2S_4$; *stibnite*, or antimony sulphide, $Sb_2S_3$; *cinnabar*, or mercury sulphide, HgS.

In combination with metals and oxygen, sulphur occurs in sulphates, such as *gypsum*, $CaSO_4$; *heavy spar*, $BaSO_4$; *kieserite*, $MgSO_4$.

**Modes of Formation.**—(1.) Sulphur is formed when sulphuretted hydrogen is brought in contact with sulphur dioxide; the two gases mutually decompose one another, with the formation of water and the precipitation of sulphur—

$$2H_2S + SO_2 = 2H_2O + 3S.$$

(2.) It is also produced when sulphuretted hydrogen is burnt with an insufficient supply of air—

$$H_2S + O = H_2O + S.$$

This reaction probably takes place in two stages, a portion of the sulphuretted hydrogen burning to sulphur dioxide, and this then reacting upon a further quantity of sulphuretted hydrogen, thus—

$$(a)\ H_2S + 3O = H_2O + SO_2.$$
$$(b)\ 2H_2S + SO_2 = 2H_2O + 3S.$$

It is supposed that some of the free sulphur found in volcanic regions, has been produced by this action of these two gases upon one another.

**Extraction of Sulphur from Native Sulphur.**—Natural sulphur is always more or less mixed with earthy or mineral tters, from which it is necessary to free it. This is usually cted by melting the sulphur and allowing it to flow away from accompanying impurities. The crude sulphur rock is stacked brick kilns having a sloping floor, and the mass ignited by roducing through openings in the heap, burning faggots of ishwood. The heat produced by the combustion of a part of the phur, causes the remainder to melt and collect upon the sloping or of the kiln, from which it can be drawn off into rough moulds. ie loss of sulphur by this method is very considerable, usually t more than two-thirds of the total amount contained in the rock ing obtained.

(3.) Sulphur may be obtained by heating certain metallic sul- ides ; thus when iron pyrites is heated it yields one-third of its lphur—

$$3FeS_2 = Fe_3S_4 + S_2.$$

If the pyrites be roasted in kilns, the whole of the sulphur is btained, partly as free sulphur, and partly as sulphur dioxide, ius—

$$3FeS_2 + 5O_2 = Fe_3O_4 + 3SO_2 + 3S.$$

This method was at one time rather extensively employed for he preparation of sulphur on a manufacturing scale, but has now ractically gone out of use, the pyrites being usually roasted with xcess of air, whereby the whole of the sulphur is converted into ulphur dioxide for use in the manufacture of sulphuric acid.

By a similar process, sulphur is obtained as a bye-product during he roasting of copper pyrites, in the first stage of the operation of opper-smelting.

(4.) Large quantities of sulphur are now extracted from the *vat-waste*, or *alkali-waste*, obtained in the manufacture of sodium arbonate by the Leblanc process. This material consists largely f an insoluble oxy-sulphide of lime, a compound containing calcium ulphide (CaS) and calcium oxide (CaO) in varying proportions. Either in the lixiviating tanks themselves, or in special vats, a urrent of air is blown through the compound, whereby the calcium ulphide it contains is ultimately converted into a mixture of calcium ydrosulphide ($CaH_2S_2$), thiosulphate ($CaS_2O_3$), and polysulphide $CaS_5$), according to the following equations—

$$(1.)\quad 2CaS + 2H_2O = CaH_2S_2 + CaH_2O_2.$$

This reaction goes forward in several stages, in the course of which a quantity of sulphur is set free; this is then acted upon by the calcium hydroxide, with the formation of calcium polysulphide and calcium thiosulphate, thus—

$$(2.)\quad 3CaH_2O_2 + 12S = 2CaS_5 + CaS_2O_3 + 3H_2O.$$

The materials are alternately oxidised and lixiviated several times, and the liquor is then treated with excess of hydrochloric acid, at a temperature of about 60°, which decomposes the various sulphur compounds according to the following equations—

$$(a.)\quad CaH_2S_2 + 2HCl = CaCl_2 + 2H_2S.$$
$$(b.)\quad CaS_5 + 2HCl = CaCl_2 + H_2S + 4S.$$
$$(c.)\quad CaS_2O_3 + 2HCl = CaCl_2 + SO_2 + S + H_2O$$

The best results are obtained, when the sulphur compounds are present in such proportions that the $SO_2$ evolved by reaction *c* is sufficient to decompose the whole of the $SH_2$ produced by the other two reactions, so that neither gas escapes—

$$SO_2 + 2H_2S = 2H_2O + 3S.$$

(5.) Sulphur is also obtained from the spent oxide of iron which has been used in the "purifiers" employed upon gas-works. Coal gas contains considerable quantities of sulphuretted hydrogen, which are removed from the gas by passing it through hydrated ferric oxide ($Fe_2H_6O_6$), which absorbs the whole of the sulphuretted hydrogen, thus—

$$Fe_2H_6O_6 + 3H_2S = 2FeS + S + 6H_2O.$$

When the compound has lost its power to absorb sulphuretted hydrogen, the material is thrown out of the purifiers and exposed to air and moisture, when the iron becomes reconverted into the hydrated oxide, and the sulphur is set free—

$$2FeS + 3O + 3H_2O = Fe_2H_6O_6 + 2S.$$

This *revivified* material is then employed for the purification of a further quantity of gas. It is found that after a certain number of revivifying operations, the substance begins to lose its power of absorbing any additional sulphuretted hydrogen, and as it then ntains nearly half its weight of sulphur, it becomes a valuable urce of this element. The sulphur is obtained from it by distiltion, or the material may be roasted in special kilns, whereby the lphur is converted into sulphur dioxide, and employed for the anufacture of sulphuric acid.

**Purification.**—The crude sulphur obtained by the foregoing ethods is purified by distillation, the process being carried out in e arrangement shown in Fig. 105. The sulphur is first melted an iron pot, *d*, and the liquid substance drawn off at will by

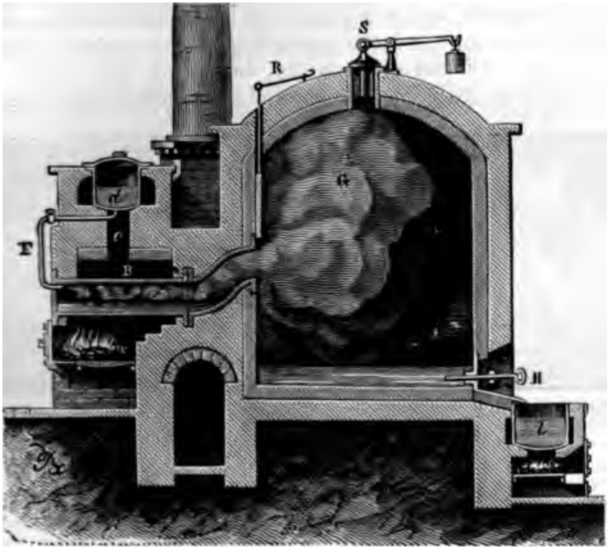


FIG. 105.

eans of the pipe F into the retort B. The sulphur is there iled by means of the fire, and the vapour allowed to issue into the rge brickwork chamber G. As the vapour enters the chamber, it ndenses upon the walls and floor in the form of a light, powdery eposit, consisting of minute crystals, and constituting the *flowers* *sulphur* of commerce. As the process continues, and the brickork becomes hot, this soft powder melts and collects upon the oor as an amber-coloured liquid, which is run out from time to time from the opening at H, and cast either into large blocks or into cylindrical rods, by means of wooden moulds. In the latter form it is known as *roll sulphur.*

When the sulphur vapour first enters the chamber and mixes with the air, the mixture frequently ignites with a feeble explosion; the chamber, therefore, is furnished with a valve, S, at the top, whereby the pressure developed at the moment of combustion may be relieved.

**Properties.**—Sulphur, as ordinarily seen, is a pale-yellow brittle crystalline solid. It is insoluble in water, but readily dissolves in carbon disulphide, and to a greater or less degree in turpentine, benzene, chloroform, sulphur chloride, and many other solvents. It is a non-conductor of electricity, and an extremely bad conductor of heat. A piece of sulphur on being very gently warmed, even by being grasped in the hand, may be heard to crack by the unequal heating, and will ultimately fall to pieces. At a temperature of 114.5 sulphur melts to a clear amber-coloured and moderately mobile liquid; on raising the temperature of this liquid its colour rapidly darkens, and at the same time it loses its mobility, until at a temperature of about 230° the mass appears almost black, and is so viscous that it can no longer be poured from the vessel. As the temperature is still further raised, the substance, while retaining its dark colour, again becomes liquid, although it does not regain its original limpidity. At 448° the liquid boils, and is converted into a pale yellowish-brown coloured vapour. On allowing the boiling sulphur to cool, it passes through the same changes in reverse order until it solidifies.

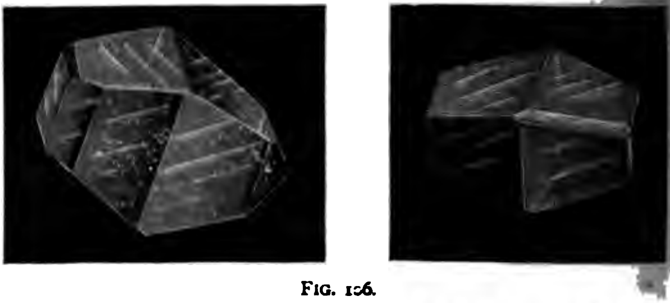


FIG. 106.

When the vapour of sulphur is heated to 1000°, it is converted nto a true gas, and has a density of 32, one litre of the gas weighng 32 criths.

Sulphur is known to exist in four allotropic modifications, two of hich are crystalline and two amorphous.

(*a*) *Rhombic Sulphur.*—Of the two crystalline varieties this is he more stable. Sulphur, therefore, that occurs native is found rystallised in this form. It may be obtained by allowing a soluion of sulphur in carbon disulphide to slowly evaporate. Fig. 106 epresents two large rhombic octahedral crystals of sulphur btained in this way.

Octahedral crystals of sulphur can also be obtained under certain conditions, when melted sulphur is allowed to crystallise. Sulphur in the liquid condition exhibits the phenomenon of suspended solidification to a very high degree, and if the liquid be carefully cooled out of contact with air, the temperature may fall to 90° before solidification takes place. If into the liquid in this state a crystal of the rhombic variety be dropped, the sulphur begins to solidify in crystals of that form. If the superfused sulphur be contained in a hermetically closed flask, the liquid frequently deposits octahedral crystals, and by allowing the mass to partially solidify, and quickly inverting the flask, the crystals may be seen upon the bottom of the vessel.

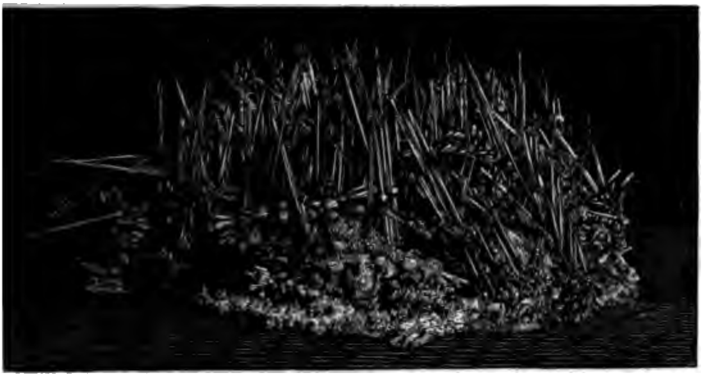


FIG. 107.

The specific gravity of this form of sulphur is 2.05.

(*β*) "*Prismatic*" *Sulphur.*— When melted sulphur is allowed to cool under ordinary conditions, such as in a crucible, or beaker, it crystallises in the form of prismatic needles, belonging to the monoclinic, or monosymmetric system. By allowing the mass to partially solidify, and pouring off the still liquid portion, these crystals will be seen lining the inside of the beaker as long translucent prisms. Fig. 107 shows such a mass of crystals. Prismatic crystals of sulphur are also obtained, when this element is crystallised from a hot solution in oil of turpentine.

The specific gravity of this form of sulphur is less than that of the octahedral variety, being 1.98.

At ordinary temperatures this modification is unstable, and in the course of a day or two the crystals lose their translucent appearance, owing to their becoming broken down into a number of smaller crystals of the rhombic variety, and present the opaque yellow appearance of ordinary roll sulphur. This change from the prismatic to the octahedral variety, which takes place more quickly when the crystals are scratched, or subjected to vibration, is attended with evolution of heat. When monoclinic sulphur is thrown into carbon disulphide, its transformation into the stable modification takes place rapidly, and in this way, by means of a thermopile, the heat evolved by the change may be rendered evident. As carbon disulphide, however, at once exerts its solvent action upon the rhombic sulphur the moment it is formed, the reduction of temperature resulting from this cause, would completely over-balance and mask the more feeble heat effect produced by the passage of the sulphur from the unstable to the stable form. In order, therefore, to render evident the heat resulting from the change of crystalline form, the carbon disulphide must be previously allowed to dissolve as much sulphur as it can take up. If a small quantity of carbon disulphide, so saturated with sulphur, be placed in a corked flask, and stood upon the face of a thermo-electric pile* in connection with a galvanometer, and a quantity of prismatic crystals of sulphur be quickly thrown into the liquid, a sensible deflection of the galvanometer needle will be seen in the direction caused by heat.

Although under ordinary conditions, monoclinic sulphur is unstable and passes into rhombic form, at temperatures between

---

[*] The thermo-electric pile is a delicate physical instrument employed for registering slight changes of temperature; for descriptions of the apparatus the student must consult text-books on physics.

100° and 114°, it appears to be the more stable variety, for at this temperature rhombic sulphur passes into the monoclinic variety.

(γ) *Plastic Sulphur.*—When sulphur which has been heated until it reaches the viscous condition, is suddenly plunged into water, or when boiling sulphur is poured in a thin stream into water, the substance solidifies to a tough elastic material somewhat resembling indiarubber. The sulphur in this form is known as *plastic sulphur.* This variety is best obtained by distilling a quantity of ordinary sulphur from a glass retort (Fig. 108), and allowing the distilled liquid to flow in a fine stream into cold water placed for its reception. As the liquid sulphur falls into the water, it congeals to the plastic condition as a continuous thread, which winds itself in a regular manner into beautiful coils of a delicate translucent amber colour. The specific gravity of plastic sulphur is 1.95, and it is not soluble in carbon disulphide. At ordinary temperatures this allotrope of sulphur is gradually transformed into the stable rhombic variety; in the course of a few days it loses its transparency and elasticity, and becomes converted into the ordinary lemon yellow brittle condition of common sulphur. This change takes place more quickly if the plastic material be stretched and worked between the fingers, and still more readily by heating it for a few moments to 100°, and allowing it again to cool.

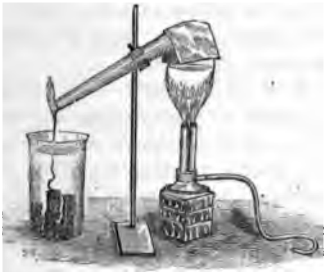


FIG. 108.

(δ) *White Amorphous Sulphur.*—When sulphur is heated, and the vapour condensed upon a cool surface, as in the formation of ordinary flowers of sulphur, although the greater portion of the sulphur is sublimed in the rhombic octahedral form, the sublimate contains a small amount of sulphur in the form of an amorphous powder, which is almost milk-white in colour.

This modification is best obtained by treating flowers of sulphur, which usually contains as much as 5 or 6 per cent. of amorphous sulphur, with carbon disulphide, whereby the rhombic variety is dissolved, and the white amorphous substance, which is insoluble in that liquid, is left behind. By filtering the liquid and washing the residue with carbon disulphide until the whole of the soluble sulphur is removed, the amorphous powder may be obtained in a state of purity.

This amorphous substance is also produced in small quantity, by the action of light upon a solution of sulphur in carbon disulphide. Thus, if a perfectly clear solution of sulphur in this liquid be placed for even a few minutes in the path of a beam of electric light, the solution will be seen to become rapidly turbid, owing to the formation of this insoluble modification.

This milk-white amorphous modification is stable at the ordinary temperature, and therefore does not pass spontaneously into the rhombic variety. When heated to a temperature of 100°, it quickly becomes yellow in colour, and is then readily soluble in carbon disulphide, having been transformed at that temperature into the ordinary stable form.

**Milk of Sulphur.**—This substance is a medicinal preparation, obtained by precipitating sulphur from a polysulphide of lime by means of hydrochloric acid. Flowers of sulphur and milk of lime are boiled together for some time, and after settling, the clear reddish liquid containing the calcium polysulphides is decanted off, and hydrochloric acid added to it; calcium chloride is formed, and sulphur in a fine state of subdivision is precipitated—

$$CaS_x + 2HCl = CaCl_2 + H_2S + (x-1)S.$$

The product so obtained is pale yellow in colour, and consists of ordinary sulphur often contaminated with considerable quantities of calcium sulphate, derived from sulphuric acid present in the hydrochloric acid employed in the precipitation.

When sulphur in any of its modifications is heated in the air, it takes fire and burns with a pale blue flame, giving rise to sulphur dioxide; when burnt in oxygen a small quantity of sulphur trioxide is at the same time produced.

Finely divided sulphur, when exposed to air and moisture, undergoes slow oxidation even at ordinary temperatures, with the formation of sulphuric acid. Thus, if flowers of sulphur be moistened with water and freely exposed to the air, in a short time the water will be distinctly acid. On this account, sulphur that is used for pyrotechnic purposes, is thoroughly washed and dried, and preserved in warm dry places.

Sulphur combines directly with many metals under the influence of heat, forming sulphides; the union in many cases being accompanied by vivid combustion. Thus, a strip of copper, when introduced into sulphur vapour, burns brilliantly with the formation of copper sulphide; and a red-hot bar of iron, when pressed against a roll of sulphur, burns in the vapour which is generated, and the molten sulphide falls in scintillating masses through the air—

$$Fe + S = FeS.$$

Heated with sodium or potassium, the alkaline sulphides are formed with deflagration—

$$K_2 + S = K_2S.$$

## *COMPOUNDS OF SULPHUR WITH HYDROGEN.*

Two compounds of these elements are known, namely—

| | |
|---|---|
| Hydrogen sulphide or sulphuretted hydrogen . | $H_2S$. |
| Hydrogen persulphide . . . . . . . | $H_2S_2$. |

### HYDROGEN SULPHIDE.

Formula, $H_2S$. Molecular weight = 34. Density = 17.

**Occurrence.**—This gas is evolved in volcanic regions, and is met with in solution in sulphur mineral waters.

**Modes of Formation.**—(1.) Sulphuretted hydrogen may be formed by the direct union of its elements, by passing a mixture of hydrogen and the vapour of sulphur through a strongly heated tube. In small quantity it is produced when hydrogen is passed into boiling sulphur, or over certain heated metallic sulphides.

(2.) Sulphuretted hydrogen is most readily obtained by the action of either hydrochloric or sulphuric acid upon ferrous sulphide, thus—

$$FeS + 2HCl = FeCl_2 + H_2S.$$
$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

The ferrous sulphide in broken fragments is placed in a two-necked bottle, similar to the apparatus, Fig. 27, employed for the preparation of hydrogen, and the dilute acid poured upon it. The gas is rapidly evolved without the application of heat. The gas obtained by this method always contains free hydrogen, owing to the presence of uncombined iron in the ferrous sulphide.

(3.) Pure sulphuretted hydrogen may be obtained by heating antimony trisulphide (grey antimony ore) with strong hydrochloric acid, when antimony trichloride is produced and hydrogen sulphide evolved—

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

(4.) Sulphuretted hydrogen is produced during the putrefaction of organic substances containing sulphur, the offensive smell of a decomposing egg being due to the presence of this gas. It is also produced during the destructive distillation of coal, by the direct union of hydrogen with the sulphur contained in the pyrites, hence coal gas always contains sulphuretted hydrogen amongst its impurities.

**Properties.**—Sulphuretted hydrogen is a colourless gas having a somewhat sickly sweetish taste, and an extremely offensive odour. It acts as a powerful poison when inhaled in the pure state, and even when very largely diluted with air it gives rise to dizziness and headache. Its poisonous effects are more marked upon some animals than others : thus, a bird was found to die in an atmosphere containing only $\frac{1}{1500}$ of sulphuretted hydrogen, while it required an amount equal to $\frac{1}{250}$ to poison a hare ; and again, cold-blooded animals are in no way affected by inhaling these proportions of the gas. Sulphuretted hydrogen is moderately soluble in water; at ordinary temperatures water dissolves about three times its own volume of the gas. In collecting it over water, therefore, considerable loss results unless the water be warm. The coefficient of absorption by water at 0° is 4.3706.

The aqueous solution gives an acid reaction with litmus, and possesses the taste and smell of the gas. It quickly decomposes on exposure to air, the hydrogen of the sulphuretted hydrogen combines with oxygen, and the liquid becomes turbid by the precipitation of sulphur. Hydrogen sulphide is an inflammable gas, burning with a bluish flame, and producing sulphur dioxide and water—

$$2H_2S + 3O_2 = 2SO_2 + 3H_2O.$$

If mixed with oxygen in the proportion demanded by this equation, viz., two volumes of sulphuretted hydrogen and three volumes of oxygen, and ignited, the mixture explodes with violence. When the gas is burned with an insufficient supply of air or oxygen for its complete combustion, the sulphur is deposited.

Sulphuretted hydrogen is decomposed by the halogens, with the deposition of sulphur, and the formation of the hydrogen compound of the halogen element, thus—

$$H_2S + Cl_2 = 2HCl + S.$$

Fluorine, chlorine, and bromine are capable of bringing about this decomposition at ordinary temperatures; in the case of iodine, the reaction is attended with absorption of heat, which may be supplied by passing the mixture of iodine vapour and sulphuretted hydrogen through a hot tube, or by causing the action to take place in the presence of water. In the latter case the heat of solution of the hydriodic acid, determines the reaction.

When passed into sulphuric acid, reduction of the acid takes place with the precipitation of sulphur—

$$H_2SO_4 + H_2S = SO_2 + 2H_2O + S.$$

Sulphuretted hydrogen, therefore, cannot be dried by means of sulphuric acid.

The gas acts upon many metals with the formation of sulphides; thus, when potassium is heated in a stream of hydrogen sulphide it readily burns and produces potassium hydro-sulphide, $H_2S + K = KHS + H$. Such metals as tin, lead, silver, &c., are rapidly tarnished in contact with this gas. On this account articles of silver, when exposed to the air of towns, quickly become covered with a film of sulphide, which first appears yellowish-brown, and gradually becomes black. The discoloration of a silver spoon, when introduced into an egg which is partially decomposed, is due to the same cause.

Sulphuretted hydrogen also acts upon metallic salts, combining with the metal to form a sulphide. The "white-lead" employed in ordinary paint is gradually blackened on prolonged exposure to the air by the formation of lead sulphide.

Hydrogen sulphide is rapidly absorbed by lime, with the formation of calcium hydrosulphide—

$$CaH_2O_2 + 2H_2S = CaH_2S_2 + 2H_2O.$$

It is also absorbed by calcium sulphide, yielding the same compound. This reaction is employed in the method known as *Chance's process*, for utilising the sulphur of the vat waste of the alkali manufacture. This consists in passing lime-kiln gases through a series of vessels containing the waste mixed with water. In the first vessels the carbon dioxide is absorbed, and sulphuretted hydrogen evolved. This, passing into the later vessels, is absorbed by the vat waste, forming calcium hydrosulphide, which in its turn is decomposed by carbon dioxide, with the evolution of twice the volume of sulphuretted hydrogen for a given volume of carbon dioxide, as in the first reaction—

$$(1)\quad CaS + CO_2 + H_2O = CaCO_3 + H_2S.$$
$$(2)\quad CaS + H_2S = CaH_2S_2.$$
$$(3)\quad CaH_2S_2 + CO_2 + H_2O = CaCO_3 + 2H_2S.$$

The sulphuretted hydrogen, mixed with atmospheric nitrogen and a small quantity of carbon dioxide, is sufficiently rich to burn, yielding sulphur dioxide, which can then be employed for the manufacture of sulphuric acid.

Sulphuretted hydrogen is also decomposed by ferric hydroxide, with the formation of ferrous sulphide and water, and the decomposition of sulphur, as described on page 362. This action takes place with the evolution of considerable heat, the temperature rising high enough to ignite a mixture of sulphuretted hydrogen and oxygen.*

Sulphuretted hydrogen is a valuable laboratory reagent, on account of the general behaviour of certain classes of sulphides. Thus, the sulphides of certain metals, being insoluble in dilute acids, are precipitated from acid solutions ; for example—

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$
$$CdCl_2 + H_2S = CdS + 2HCl.$$

Others are soluble in acids, but insoluble in alkaline liquids, and are therefore precipitated by sulphuretted hydrogen in the presence of ammonia, or by the addition of ammonium sulphide, thus—

$$ZnSO_4 + (NH_4)_2S = ZnS + (NH_4)_2SO_4.$$

A third group of metals yield sulphides that are soluble in water, and therefore are not separated either in acid or alkaline solutions.

Many of the metallic sulphides are also possessed of characteristic colours, which readily serve for their identification. Thus, arsenious sulphide is pale yellow, and cadmium sulphide golden yellow. Antimonious sulphide has a bright red colour, while zinc sulphide is white.

This behaviour of metals towards sulphuretted hydrogen is the basis upon which certain methods of qualitative analyses are founded.

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* "Chemical Lecture Experiments," No. 559.

## HYDROGEN PERSULPHIDE.

Formula, $H_2S_2$.

**Modes of Formation.**—(1.) This substance, which stands in the same relation to hydrogen sulphide, as hydrogen peroxide does to water, may be obtained, by slowly pouring a solution of calcium disulphide into hydrochloric acid, in the cold; the liquids being rapidly stirred during the process of mixing, and the acid being kept in considerable excess—

$$CaS_2 + 2HCl = CaCl_2 + H_2S_2.$$

The hydrogen persulphide separates out as a heavy, pale yellow, oily compound, which settles to the bottom of the liquid. The calcium disulphide is prepared by boiling together one part of lime with about twenty parts of water, and one part of flowers of sulphur. The yellow liquid that is obtained will contain more or less of the higher sulphides of lime, and in proportion as these are present there will be a precipitation of sulphur with the hydrogen persulphide, thus—

$$CaS_5 + 2HCl = CaCl_2 + H_2S_2 + 3S.$$

(2.) Hydrogen persulphide may also be obtained from a compound that is produced by the action of sulphuretted hydrogen upon strychnine, in the presence of oxygen—

$$2C_{21}H_{22}N_2O_2 + 6SH_2 + 3O = 3H_2O + 2C_{21}H_{22}N_2O_2,3H_2S_2.$$

This substance, on treatment with an acid, yields the persulphide.

**Properties.**—Hydrogen persulphide is an oily liquid having a specific gravity of 1.73. It has a pungent smell, accompanied by the odour of sulphuretted hydrogen, due probably to the partial decomposition of the compound, and its vapour is irritating to the eyes. It is an unstable substance, decomposing at ordinary temperatures into sulphur and sulphuretted hydrogen: when heated, this decomposition takes place rapidly. It readily dissolves sulphur, and on this account, and the readiness with which the compound decomposes, it is extremely difficult to obtain it in a state of purity, and so to determine its exact composition. It is insoluble in water, but dissolves readily in carbon disulphide and ether: its solution in the former liquid is more stable than the liquid substance itself.

Hydrogen persulphide burns with a blue flame, yielding sulphur dioxide and water.

Hydrogen persulphide possesses feeble bleaching properties, and like its oxygen analogue it is decomposed by certain metallic oxides, with the evolution of sulphuretted hydrogen.

## *COMPOUNDS OF SULPHUR WITH CHLORINE.*

Two of these compounds exist at ordinary temperatures, while a third is only known at temperatures below – 22°.

| | |
|---|---|
| 1. Disulphur dichloride or sulphothionyl chloride | $S_2Cl_2$. |
| 2. Sulphur dichloride . . . . . . . | $SCl_2$. |
| 3. Sulphur tetrachloride . . . . . . | $SCl_4$. |

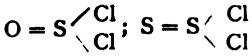
**Disulphur Dichloride,** $S_2Cl_2$.—This substance is obtained by passing dry chlorine over the surface of heated sulphur, contained in a retort; the compound, which distils away as fast as it is formed, condenses in the receiver as a yellow liquid—

$$S_2 + Cl_2 = S_2Cl_2.$$

**Properties.**—The redistilled liquid is an amber-coloured fuming substance with a disagreeable penetrating odour, the vapour of which irritates the eyes. Its specific gravity is 1.709, and it boils at 138.1°. In contact with water it gradually decomposes into hydrochloric acid and sulphur dioxide, with the precipitation of sulphur. The action takes place in two stages, thiosulphuric acid being formed as an intermediate product, thus—

$$(\alpha.)\ 2S_2Cl_2 + 3H_2O = 4HCl + S_2 + H_2S_2O_3.$$
$$(\beta.)\ H_2S_2O_3 = H_2SO_3 + S.$$

Disulphur dichloride dissolves sulphur with great readiness, and the solution so obtained is largely employed in the process of vulcanising indiarubber.

This compound is the most stable of the three chlorides of *sulphur*. From the fact that it contains chlorine and sulphur in the proportion of one atom of each element, it is sometimes called sulphur monochloride; but as its vapour density (67.4) shows that it contains two atoms of each element in the molecule, the use of the word monochloride is calculated to mislead. The name sulphothionyl chloride indicates its analogy to thionyl chloride, $SOCl_2$, from which it may be regarded as being derived, by the replacement of the oxygen by an atom of sulphur,  $O = S\begin{matrix}\diagup Cl \\ \diagdown Cl\end{matrix}$; $S = S\begin{matrix}\diagup Cl \\ \diagdown Cl\end{matrix}$

**Sulphur Dichloride,** $SCl_2$.—This compound is obtained by passing a stream of dry chlorine into disulphur dichloride at a temperature not above 0°. When the maximum amount of chlorine is absorbed, the liquid assumes a dark reddish-brown colour. Excess of chlorine is removed by passing a stream of carbon dioxide through the liquid.

Sulphur dichloride rapidly dissociates with rise of temperature into free chlorine and disulphur dichloride; at +20° this decomposition amounts to 6.5 per cent., at 50° 24.59 per cent., and at 100° 80.85 per cent. On boiling the compound, therefore, chlorine is evolved, and the disulphur dichloride remains behind.

In contact with water it is decomposed in the same manner as the more stable compound.

**Sulphur Tetrachloride,** $SCl_4$.—This compound only exists at temperatures below −22°, and is produced by saturating sulphur dichloride with chlorine at that temperature. It dissociates very rapidly as the temperature rises; thus, at 7° above the temperature at which it is formed, viz., at −15°, this decomposition amounts to 58.05 per cent. At −2° 88.07 per cent. of the compound dissociates, while at +6.2 the percentage rises to 97.57.

The compound is decomposed by water with violence into sulphur dioxide and hydrochloric acid—

$$SCl_4 + 2H_2O = SO_2 + 4HCl.$$

**Compounds of Sulphur with Bromine and Iodine** have been obtained, corresponding to $S_2Cl_2$. $S_2Br_2$ as a red-coloured liquid, boiling with partial decomposition at 200°; and $S_2I_2$ as a dark-grey crystalline solid, which melts at a temperature about 60°.

## *OXIDES AND OXYACIDS OF SULPHUR.*

Four oxides of sulphur are known, namely—

| | |
|---|---|
| (1.) Sulphur dioxide (sulphurous anhydride) . | $SO_2$. |
| (2.) Sulphur trioxide (sulphuric anhydride) . | $SO_3$. |
| (3.) Sulphur sesquioxide . . . . . | $S_2O_3$. |
| (4.) Persulphuric anhydride . . . . . | $S_2O_7$. |

Three of these oxides, namely, Nos. 1, 2, 4, give rise respectively to the three acids, sulphurous, sulphuric, and persulphuric, besides which several others are known—

| | | |
|---|---|---|
| Hyposulphurous acid . . . . | $H_2SO_2$ | $\left.\begin{matrix}HO\\HO\end{matrix}\right\}S.$ |
| Sulphurous acid . . . . . | $H_2SO_3$ | $\left.\begin{matrix}HO\\HO\end{matrix}\right\}SO.$ |
| Sulphuric acid . . . . . . | $H_2SO_4$ | $\left.\begin{matrix}HO\\HO\end{matrix}\right\}SO_2$ |
| Persulphuric acid . . . . . | $HSO_4$* | $\left.\begin{matrix}HO\\O\end{matrix}\right\}SO_2$ |
| Thiosulphuric acid† . . . . . | $H_2S_2O_3$ | $\left.\begin{matrix}HO\\HS\end{matrix}\right\}SO_2$ |
| Pyrosulphuric acid (Nordhausen sulphuric acid) . . . . | $H_2S_2O_7$ | $\left.\begin{matrix}HO.SO_2\\HO.SO_2\end{matrix}\right\}O.$ |

Besides these acids, there is a series known under the general name of the polythionic acids. They may be regarded as being derived from dithionic acid, which is the first of the series, by the absorption into the molecule of various quantities of sulphur. Four of these acids are believed to exist, viz. :—

| | | |
|---|---|---|
| Dithionic acid (sometimes called hyposulphuric acid) . . . | $H_2S_2O_6$ | $\left.\begin{matrix}HO.SO_2\\HO.SO_2\end{matrix}\right\}$ |
| Trithionic acid . . . . . . | $H_2S_3O_6$ | $\left.\begin{matrix}HO.SO_2\\HO.SO_2\end{matrix}\right\}S.$ |
| Tetrathionic acid . . . . . | $H_2S_4O_6$ | $\left.\begin{matrix}HO.SO_2\\HO.SO_2\end{matrix}\right\}S_2$ |
| Pentathionic acid . . . . . | $H_2S_5O_6$ | $\left.\begin{matrix}HO.SO_2\\HO.SO_2\end{matrix}\right\}S_3$ |

## SULPHUR DIOXIDE.

Formula, $SO_2$. Molecular weight = 63.92. Density = 31.96.

**Occurrence.**—This compound is met with in the gaseous emanations from volcanoes, and in solution in certain volcanic springs. It is also present in the air of towns, being derived from the combustion of the sulphur compounds present in coal.

**Modes of Formation.**—(1.) Sulphur dioxide is formed when sulphur burns in air or oxygen—

$$S + O_2 = SO_2.$$

---

* By some chemists— $H_2S_2O_8$, $\left.\begin{matrix}HO.SO_2\\HO.SO_2\end{matrix}\right\}O_2$.

† This acid is sometimes incorrectly called *hyposulphurous acid*, its sodium salt being known as *sodium hyposulphite*: the so-called "hypo" of the photographers.

At the same time small quantities of sulphur trioxide are formed, which render the gas obtained by this combustion more or less foggy.

(2.) Sulphur dioxide may also be obtained by heating sulphur with a metallic peroxide, such as manganese dioxide, thus—

$$S_2 + MnO_2 = SO_2 + MnS.$$

(3.) It is obtained when such metallic sulphides as copper pyrites or iron pyrites are roasted in a current of air, the metal being converted into oxide, thus—

$$2FeS_2 + 11O = Fe_2O_3 + 4SO_2.$$

(4.) The most convenient laboratory process for preparing sulphur dioxide consists in heating sulphuric acid with copper, the final products of the reaction being copper sulphate, water, and sulphur dioxide—

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$

The metals mercury or silver may be substituted for copper, but in practice the latter metal is usually employed.

(5.) Sulphur dioxide is also formed when sulphuric acid is heated with sulphur, the oxidation of the sulphur and the reduction of the sulphuric acid going on simultaneously—

$$S + 2H_2SO_4 = 2H_2O + 3SO_2.$$

(6.) The reduction of sulphuric acid may be brought about by means of carbon; thus, if sulphuric acid be heated with carbon, the latter is oxidised to carbon dioxide, and the acid is reduced to sulphur dioxide—

$$C + 2H_2SO_4 = 2H_2O + 2SO_2 + CO_2.$$

This method is employed on a large scale for the preparation of alkaline sulphites. The carbon dioxide which accompanies the sulphur dioxide, not being soluble to any extent in water containing sulphurous acid, is not in any way detrimental.

(7.) Sulphur dioxide is formed by the decomposition of a sulphite by dilute sulphuric acid, thus—

$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + H_2O + SO_2.$$

**Properties.**—Sulphur dioxide is a colourless gas, having the well-known suffocating smell usually associated with burning sulphur. The gas will not burn in the air, nor will it support the combustion of ordinary combustibles: a taper introduced into the gas is instantly extinguished. Sulphur dioxide is more than twice as heavy as air, its specific gravity being 2.211 (air = 1). On this account it is readily collected by displacement: it cannot be collected over water on account of its solubility in that liquid, but may be collected over mercury. The solubility of sulphur dioxide in water at various temperatures is seen by the following figures—

| | | | | | | |
|---|---|---|---|---|---|---|
| 1 vol. of water | at | 0° | dissolves | 79.789 | vols. | $SO_2$. |
| ” | ” | 20° | ” | 39.374 | ” | |
| ” | ” | 40° | ” | 18.766 | ” | |

The solution is strongly acid, and is regarded as sulphurous acid, the gas having entered into chemical union with the water—

$$SO_2 + H_2O = H_2SO_3.$$

On cooling a saturated solution of sulphur dioxide to 0°, a solid crystalline hydrate is deposited, having the composition $H_2SO_3$, $8H_2O$.*

When the solution is boiled, the whole of the sulphur dioxide is expelled.

Sulphur dioxide is an easily liquefied gas. At 0° a pressure of 1.53 atmospheres is sufficient to condense it, while at ordinary pressures it may be liquefied by a cold of − 10°. Its critical temperature is 155.4°.

To obtain liquid sulphur dioxide, the gas, as evolved from the action of sulphuric acid upon copper, is dried by being passed through a bottle containing sulphuric acid, and is then passed through a gas-condensing tube, Fig. 109, immersed in a freezing mixture. The gas at once condenses in the bulb of the apparatus, as a colourless, transparent, mobile liquid, which boils at − 8°. When the liquid is cooled to − 76° it solidifies to a transparent, ice-like mass.

Liquid sulphur dioxide is largely employed as a refrigerating agent, low temperatures being obtained by its rapid evaporation under reduced pressure. The liquid dissolves phosphorus, iodine, sulphur, and many resins. When thrown upon water, a portion of the liquid dissolves, and, owing to the reduction of temperature caused by the rapid evaporation of the remainder, a quantity of the water is frozen. The ice so produced contains a large proportion of the solid hydrate $H_2SO_3,8H_2O$.

---

* Several cryohydrates of sulphurous acid have been obtained, $H_2SO_3.6H_2O$ $H_2SO_3.10H_2O$; $H_2SO_3.14H_2O$.

Although sulphur dioxide is incapable of supporting the combustion of ordinary combustibles, many metals will take fire and burn when heated in the gas. Thus, when finely-divided iron is heated in a stream of sulphur dioxide it burns, forming sulphide and oxide of the metal.

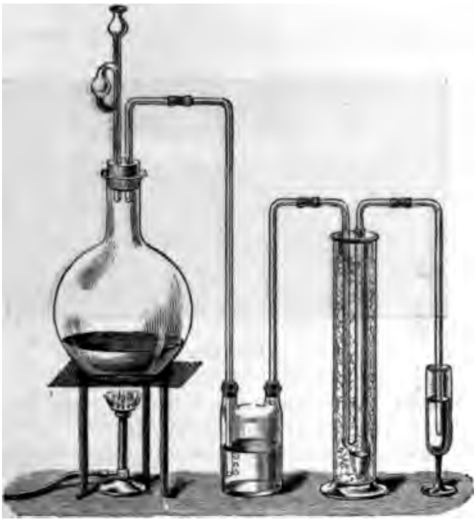


FIG. 109.

It also unites with many metallic peroxides, and often with so much energy as to give rise to light and heat. Thus, when passed over peroxide of lead, the mass glows spontaneously in the gas, and lead sulphate is produced—

$$PbO_2 + SO_2 = PbSO_4.$$

Sulphur dioxide is decomposed by the influence of strong light.

If a concentrated beam of electric light be passed through a ves filled with gaseous sulphur dioxide, the gas at first will appe perfectly transparent and clear; but in the course of a few min the track of the beam will become more and more visible as traverses the gas, owing to the formation of thin clouds of sulp trioxide and sulphur, until the atmosphere of the vessel appe to be filled with fog (Fig. 110)—

$$3SO_2 = 2SO_3 + S.$$

After the lapse of a short time, if the vessel be removed fro

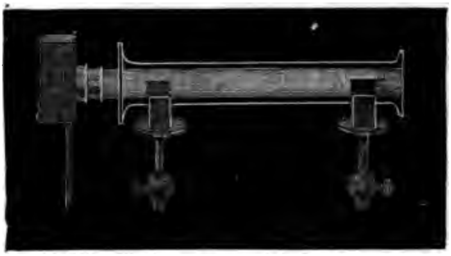


FIG. 110.

the strong light, the atmosphere will once more become clear, owing to the reformation of sulphur dioxide.

Sulphur dioxide possesses powerful bleaching properties, when in the presence of water. Its bleaching action is due to its absorption of oxygen from water, and consequent liberation of hydrogen, thus—

$$SO_2 + 2H_2O = H_2SO_4 + H_2.$$

The hydrogen so set free reduces the colouring-matter, with the formation of colourless compounds: the action in this case being the reverse to that which takes place with chlorine. In some instances, the bleaching is due to the formation of a colourless compound, by the direct combination of sulphur dioxide with the colouring-matter, as the original colour may often be restored by treatment with dilute sulphuric acid, or by weak alkaline solutions. Thus, by passing sulphur dioxide into an infusion of rose leaves, the red colour of the liquid is quickly discharged, but on the addition of a small quantity of sulphuric acid the colour is restored.

Sulphur dioxide is employed in bleaching materials that would be injured by exposure to chlorine, such as straw, silk, wool, sponge, &c., and the familiar yellow colour which gradually comes over a sponge or a piece of bleached flannel when it is washed with soap, is an illustration of the power of alkalies to restore the original colour to materials that have been bleached by this substance.

In the presence of water, sulphur dioxide converts chlorine into hydrochloric acid, and on this account is employed as an "antichlor"—

$$SO_2 + 2H_2O + Cl_2 = 2HCl + H_2SO_4.$$

In the same way it acts upon iodine, with the formation of hydriodic acid—

$$SO_2 + 2H_2O + I_2 = 2HI + H_2SO_4.$$

In the case of iodine, however, this reaction only takes place when a certain degree of dilution is maintained, for in a more concentrated condition sulphuric acid is reduced by hydriodic acid, into sulphur dioxide, according to the reverse equation, thus—

$$H_2SO_4 + 2HI = I_2 + 2H_2O + SO_2.$$

It has been shown* that aqueous sulphurous acid can only be completely oxidised by iodine, as indicated in the former equation, when the proportion of sulphur dioxide does not exceed 0.05 per cent.: when the amount exceeds this proportion the second reaction comes into operation.

Sulphur dioxide brought into contact with iodic acid, or an iodate, is oxidised into sulphuric acid and liberates iodine, thus—

$$2HIO_3 + 4H_2O + 5SO_2 = 5H_2SO_4 + I_2.$$

This reaction is made use of, as a method for the detection of the presence of sulphur dioxide. Paper which has been moistened with a solution of potassium iodate and starch, on exposure to sulphur dioxide is at once turned blue, owing to the liberated iodine combining with the starch.

---

* Bunsen.

The composition of sulphur dioxide may be determined by the combustion of sulphur in a measured volume of oxygen, in the apparatus employed for showing the volume composition of carbon dioxide (Fig. 64). After the fragment of sulphur has burnt, and the apparatus has been allowed to cool, it will be seen that there is no alteration in the volume of the contained gas; the sulphur dioxide produced, occupying the same volume as the oxygen used in its formation. Sulphur dioxide, in other words, contains its own volume of oxygen. One molecule, therefore, of sulphur dioxide contains one molecule of oxygen, weighing 31.92. But the molecular weight of sulphur dioxide is 63.92; therefore $63.92 - 31.92 = 32 =$ the weight of sulphur contained in the molecule of the gas. Sulphur dioxide, therefore, contains in the molecule one atom of sulphur, combined with two atoms of oxygen, hence its composition is expressed by the formula $SO_2$.

**Sulphurous Acid and Sulphites.**—Sulphurous acid is only known in solution and in its cryohydrates. The solution smells of sulphur dioxide, and gradually undergoes decomposition by absorption of oxygen. The acid is dibasic, having two atoms of hydrogen replaceable by metals: it is therefore capable of forming two series of salts, according to whether one or both of the hydrogen atoms are replaced. Thus, by its action upon potassium hydroxide, when the acid is in excess the so-called acid potassium sulphite, or hydrogen potassium sulphite, is obtained—

$$KHO + H_2SO_3 = H_2O + HKSO_3.$$

Whereas, if the metallic hydroxide be in excess, the normal potassium sulphite is formed—

$$2KHO + H_2SO_3 = 2H_2O + K_2SO_3.$$

The alkaline sulphites are readily soluble in water, all other normal sulphites being either difficult of solution or insoluble.

### SULPHUR TRIOXIDE.

Formula, $SO_3$. Molecular weight = 79.88. Vapour density = 39.93.

**Modes of Formation.**—(1.) This compound is produced, when a mixture of sulphur dioxide and oxygen is passed over heated spongy platinum or platinised asbestos—

$$SO_2 + O = SO_3.$$

On leading the product through a well-cooled receiver, the sulphur trioxide condenses in white silky needles. This method has been successfully employed on a commercial scale. The mixture of sulphur dioxide and oxygen, is obtained by allowing ordinary strong sulphuric acid to drop into earthenware retorts heated to bright redness, whereby it is almost entirely broken up into these two gases and water, thus—

$$H_2SO_4 = SO_2 + O + H_2O.$$

The gases are then deprived of the water, by passage first through a condenser, and then through a leaden tower containing coke moistened with sulphuric acid, and are finally passed over heated platinised asbestos contained in glazed earthenware pipes.

(2.) Sulphur trioxide is most conveniently obtained by gently heating pyrosulphuric acid in a glass retort. The trioxide distils over and may be collected in a well-cooled receiver—

$$H_2S_2O_7 = H_2SO_4 + SO_3.$$

(3.) It may also be obtained by heating sodium pyrosulphate to bright redness—

$$Na_2S_2O_7 = Na_2SO_4 + SO_3.$$

The sodium pyrosulphate is produced when hydrogen sodium sulphate (so-called *bisulphate of soda*) is heated to about 300°, thus—

$$2HNaSO_4 = H_2O + Na_2S_2O_7.$$

And on account of this origin it is sometimes termed *anhydrous sodium bisulphate*.

(4.) Sulphur trioxide can also be produced by the action of phosphorus pentoxide upon sulphuric acid. This most powerful dehydrating substance withdraws from the sulphuric acid the elements of water, when gently heated, thus—

$$H_2SO_4 + P_2O_5 = 2HPO_3 + SO_3.$$

The trioxide is distilled from the mixture, and the metaphosphoric acid remains in the retort.

**Properties.**—Sulphur trioxide is a white, silky-looking, crystalline substance, which melts at 14.8° and boils at 46°. It is very volatile, and gives off dense white fumes in contact with air, owing to the combination of its vapour with atmospheric moisture to form sulphuric acid. It combines with water with great energy to form sulphuric acid; a fragment of the compound dropped into water dissolves with a hissing sound resembling the quenching of red-hot iron—

$$SO_3 + H_2O = H_2SO_4.$$

When brought in contact with the skin, or other organic matter containing hydrogen and oxygen, it abstracts these elements and produces a burnt or charred effect upon the substance. Sulphur trioxide unites directly with barium oxide, BaO, and if the baryta be dry, the mass becomes incandescent owing to the heat of the union, and barium sulphate is formed—

$$BaO + SO_3 = BaSO_4.$$

When the vapour of sulphur trioxide is passed through a red-hot tube, it is broken down into sulphur dioxide and oxygen.

When the trioxide is heated, it melts to a colourless liquid, which exhibits a remarkably high rate of expansion by heat; between 25° and 45° its mean coefficient of expansion is 0.0027, nearly three-fourths of the expansion coefficient of a gas.

**Sulphur Sesquioxide,** $S_2O_3$.—A solution of this compound in fuming sulphuric acid was obtained early in the century by heating flowers of sulphur with Nordhausen sulphuric acid, whereby a blue solution was obtained. The substance may be prepared by the gradual addition of dry flowers of sulphur to melted sulphur trioxide, at a temperature just above its melting-point, when a malachite-green crystalline solid separates out.

The compound is unstable at ordinary temperatures, being resolved into sulphur dioxide and sulphur, the decomposition taking place rapidly upon gently warming—

$$2S_2O_3 = S + 3SO_2.$$

If the sesquioxide be sealed up in a bent glass tube and gently warmed, the sulphur dioxide may be obtained liquid in one limb of the tube.

### PERSULPHURIC ANHYDRIDE.

Formula, $S_2O_7$.

This compound is formed when a mixture of dry sulphur dioxide and oxygen is subjected to the silent electric discharge, in an ozone tube, or by treating sulphur trioxide and oxygen in the same manner. At the end of some hours a small quantity of a viscous liquid collects upon the walls of the glass vessel, which when cooled, solidifies in the form of long transparent needle-shaped crystals, resembling sulphur trioxide in appearance. It is a very unstable substance, and can only be preserved a short time even at low temperatures. It is soluble in water, with the formation of persulphuric acid, but the solution rapidly undergoes decomposition into oxygen and sulphuric acid—

$$S_2O_7 + H_2O = 2HSO_4.$$
$$2HSO_4 + H_2O = 2H_2SO_4 + O.$$

When very gently warmed, persulphuric anhydride rapidly breaks up into sulphur trioxide and oxygen—

$$S_2O_7 = 2SO_3 + O.$$

The readiness with which it gives up oxygen, constitutes this compound a powerful oxidising agent, and affords the clue to most of its reactions.

**Persulphuric Acid and Persulphates.**—When dilute sulphuric acid is subjected to electrolysis (as in the process commonly spoken of as the *electrolysis of water*), appreciable quantities of persulphuric acid are found in solution at the positive electrode, or anode.

The acid itself has never been obtained in a state of purity, its aqueous solution rapidly undergoing decomposition, as already mentioned.

In solution this compound displays all the oxidising properties of the oxide.

The potassium salt may be obtained by the electrolysis of a saturated solution of hydrogen potassium sulphate in a divided cell, the action being due to the oxidation of the hydrogen potassium sulphate by the nascent oxygen developed at the anode, thus—

$$2HKSO_4 + O = H_2O + 2KSO_4.$$

The potassium persulphate, being a sparingly soluble salt, crystallises out, and may be freed from the acid sulphate by recrystallisation.

The ammonium salt, $NH_4SO_4$, and the barium salt, $Ba(SO_4)_2,4H_2O$, have also been obtained. Barium persulphate is soluble in water, being much more readily dissolved than the potassium salt; thus, 100 parts of water at 0° dissolve 1.77 parts of potassium persulphate and 52.2 parts of the barium salt. On this account solutions of persulphates give no precipitate with barium chloride, whereby they are distinguished from sulphates: if the mixture be warmed, however, the persulphate is decomposed into a sulphate, with evolution of chlorine, thus—

$$2KSO_4 + BaCl_2 = Ba(SO_4)_2 + 2KCl = BaSO_4 + K_2SO_4 + Cl_2.$$

In the solid condition the persulphates are stable salts, but their aqueous solutions gradually evolve oxygen and become converted into sulphates—

$$2KSO_4 + H_2O = 2HKSO_4 + O.$$

The reactions exhibited by solutions of persulphates are those of strong oxidising agents.

**Hyposulphurous Acid,*** $H_2SO_2$.—This compound is obtained by the reduction of sulphurous acid by means of nascent hydrogen. Thus, when zinc is acted upon by an aqueous solution of sulphurous acid, no hydrogen is evolved, as the nascent gas combines with oxygen of the acid to form water—

$$H_2SO_3 + H_2 = H_2O + H_2SO_2.$$

The solution so obtained, has a yellowish colour, and possesses powerful reducing and bleaching properties.

Sodium hyposulphite ($HNaSO_2$) may be obtained by the action of zinc upon a cooled concentrated solution of hydrogen sodium sulphite ($HNaSO_3$), air being carefully excluded, a double sulphite of sodium and zinc being at the same time produced, thus—

$$3HNaSO_3 + Zn = HNaSO_2 + Na_2SO_3,ZnSO_3 + H_2O.$$

The greater part of the double sodium-zinc sulphite is deposited as crystals, the rest is removed by adding to the mother liquor about four times its volume of alcohol, in a closed flask. The double salt, being less soluble in alcohol than the hyposulphite, is first deposited, and the clear liquid, after being poured off and corked up, is cooled, when it solidifies to a mass of crystals of nearly pure sodium hyposulphite. The crystals in the wet condition are rapidly oxidised on exposure to air; but if quickly pressed between blotting-paper and dried in vacuo, the dry salt is not acted upon by atmospheric oxygen.

The acid is obtained from the sodium salt, by the action upon it of oxalic acid.

Sodium hyposulphite is also formed when a solution of hydrogen sodium sulphite is subjected to electrolysis, the nascent hydrogen developed at the negative electrode reducing the sulphite to hyposulphite, by the abstraction of one atom of oxygen.

**Properties.**—Hyposulphurous acid is an extremely unstable, yellow-coloured liquid, which rapidly decomposes, first into thiosulphuric acid and water, and finally into sulphur dioxide, water, and sulphur—

$$2H_2SO_2 = H_2S_2O_3 + H_2O.$$
$$H_2S_2O_3 = SO_2 + H_2O + S.$$

The acid reduces salts of silver or mercury, with precipitation of the metal, thus—

$$HgCl_2 + H_2O + H_2SO_2 = Hg + 2HCl + H_2SO_3.$$

---

* This compound (sometimes called *hydrosulphurous* acid) must not be confounded with thiosulphuric acid, which is often incorrectly called *hyposulphurous* acid (page 396).

The sodium salt possesses the same bleaching and reducing powers as the acid; and when wet, or in solution, it rapidly absorbs oxygen from the air and is converted into hydrogen sodium sulphite—

$$HNaSO_2 + O = HNaSO_3.$$

## SULPHURIC ACID.

Formula, $H_2SO_4$.

**Modes of Formation.**—(1.) This acid is formed when sulphur trioxide is dissolved in water—

$$SO_3 + H_2O = H_2SO_4.$$

(2.) It is also formed by the direct union of sulphur dioxide with hydrogen peroxide—

$$SO_2 + H_2O_2 = H_2SO_4.$$

(3.) An aqueous solution of sulphur dioxide gradually absorbs oxygen, and is converted into sulphuric acid—

$$H_2SO_3 + O = H_2SO_4.$$

(4.) **Manufacture of Sulphuric Acid.**—Sulphur dioxide is unable to absorb an additional atom of oxygen, and so pass into sulphur trioxide, without the aid of some third substance, which can act as a catalytic agent, or a carrier of oxygen. The material which is employed for this purpose, in the process by which sulphuric acid is manufactured, is one of the oxides of nitrogen, which is capable of giving up oxygen to the sulphur dioxide, and of again taking up oxygen from the air. Thus, nitrogen peroxide ($NO_2$), by the loss of one atom of oxygen, is reduced to nitric oxide, NO; which in its turn combines with atmospheric oxygen, and is reconverted into nitrogen peroxide. Therefore, when sulphur dioxide and oxygen are mixed with nitrogen peroxide in the presence of steam, a series of reactions takes place, the final result of which is that the oxygen is caused to combine with the sulphur dioxide and water, with the formation of sulphuric acid—

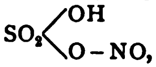
$$SO_2 + O + H_2O = H_2SO_4.$$

The nitrogen peroxide at the end of the reaction is unchanged, and is able to react in the same series of changes over and over again, thus transforming, theoretically, an unlimited, and, in practice, a relatively large quantity of sulphur dioxide into sulphuric acid.

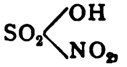
The series of changes that gives rise to the ultimate product is the following :—The sulphur dioxide, nitrogen peroxide, and water give rise, in the first place, to the formation of nitro-sulphonic acid and a molecule of nitric oxide—

$$(1.)\quad 2SO_2 + 3NO_2 + H_2O = 2H(NO)SO_4 + NO.$$

Nitro-sulphonic acid (sometimes called *nitro-sulphuric acid*, and *nitrosyl sulphate*) may be regarded as sulphuric acid in which one of the hydrogen atoms is replaced by the group (NO), thus,



$SO_2\begin{cases}OH\\O-NO,\end{cases}$ in which case the nitrogen is linked to the sulphur by the intervention of oxygen : or it may be considered as derived from sulphuric acid by the replacement of one of the groups (HO) by the group $NO_2$,



$SO_2\begin{cases}OH\\NO_2,\end{cases}$ when the nitrogen is directly attached to the sulphur. The substance is a white crystalline compound, which in the presence of water is instantly decomposed into sulphuric acid and a mixture of nitric oxide and nitrogen peroxide, thus—

$$(2.)\quad 2SO_2(HO)(NO_2) + H_2O = 2H_2SO_4 + NO + NO_2.$$

The nitric oxide in this and the former reaction, on coming in contact with the atmospheric oxygen, is at once reconverted into nitrogen peroxide—

$$(3.)\quad NO + O = NO_2.$$

In the process of the manufacture, the crystalline compound $SO_2(HO)(NO_2)$ (known as *chamber crystals*) is not actually isolated, unless from accidental causes the supply of water is in deficit, the production of these crystals being regarded as an indication that the process is not being well carried out.

The formation of sulphuric acid by these reactions, with the intermediate production of the chamber crystals, may be carried out on a small scale by means of the apparatus shown in Fig. 111. A large flask, F, is fitted with a cork, through which pass five tubes : three of these are connected to separate two-necked bottles containing sulphuric acid, through which can be delivered respectively, nitric oxide, sulphur dioxide, and oxygen. The fourth tube is attached to a flask in which water may be boiled, and through which oxygen can be passed, and the fifth tube (not shown in the figure) serves as an exit. A quantity of oxygen is first passed into the large flask through the drying-bottle D, and sufficient nitric oxide is then allowed to enter, to form deep red vapours; at the same time sulphur dioxide is passed in through the bottle S. In order to introduce a small quantity of moisture, oxygen is allowed to enter through the flask of boiling water, and in a few moments large white crystals begin to form all over the interior of the flask, and rapidly spread until the whole surface is covered.

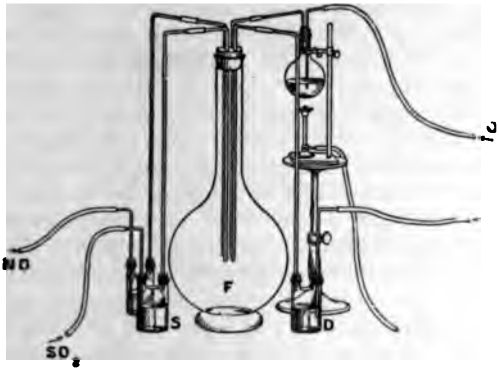


FIG. 111.

In order to show the second reaction in the cycle, the gaseous contents of the flask may be swept out by means of a rapid stream of oxygen, passed in through the drying-bottle D; and when the atmosphere within the apparatus is colourless, a quantity of steam is driven in from the small flask. The chamber crystals will be seen to dissolve with effervescence, and the flask once more becomes filled with brown fumes. The nitric oxide evolved by the decomposition of the nitrosyl sulphate, coming in contact with the oxygen within the flask, at once regenerates nitrogen peroxide, in accordance with equation No. 3.

The solution formed in the flask will be found to yield a precipitate of barium sulphate, on the addition to it of a soluble barium salt.

On a manufacturing scale, the combination of the reacting gases and vapours which gives rise to the sulphuric acid, takes place in large leaden chambers, usually about 100 feet long, 25 feet wide, and 20 feet high, having therefore a capacity of 50,000 cubic feet; several of such chambers being placed in series. Into these chambers there is delivered sulphur dioxide, air, oxides of nitrogen, and steam.

The plant employed for the manufacture of sulphuric acid consists broadly of four parts. 1. Apparatus for generating sulphur dioxide. 2. Apparatus for producing oxides of nitrogen. 3. Apparatus for absorbing oxides of nitrogen from the gases leaving the chambers. 4. The chambers in which the reactions are made.

(1.) *Pyrites Burners.*—The sulphur dioxide is obtained either by burning native sulphur, or roasting the "spent oxide" of the gas works (see Sulphur), or by roasting pyrites, the latter being the most general method. The pyrites burner, Fig. 112, B, is essentially a small furnace or kiln in which the ore is heated, and in which the admission of air can be duly regulated; as not only is it necessary to admit sufficient air to completely burn the whole of the sulphur, and so prevent any volatilisation of it in an unburnt condition, but also to supply the requisite volume of oxygen for the requirements of the reactions which are to go on within the chamber. Too large a volume of air must be avoided, in order not to unduly dilute the chamber gases.

(2.) If no loss of nitrogen peroxide took place during the cycle of changes, the same quantity of this gas would convert an infinite amount of sulphur dioxide and water into sulphuric acid; but in practice, owing to leakage, defective absorption, and the reduction of a certain percentage of this compound into nitrous oxide, it is necessary to constantly replenish the supply. This is usually done by generating a small quantity of nitric acid (by the action of sulphuric acid upon nitre) in earthenware pots, which are usually placed in an enlarged part of the flue of the pyrites burner, known as the "nitre oven," and which is provided with a door for the introduction of the pots, Fig. 112, N. The heated gases playing upon these pots, promotes the evolution of the nitric acid, which in contact with sulphur dioxide is at once decomposed according to the equation—

$$2HNO_3 + SO_2 = H_2SO_4 + 2NO_2.$$

It is found that to make up for the loss of nitrogen peroxide, out three to four parts of nitre are required for every 100 parts sulphur, burnt as pyrites.

(3.) The apparatus for the absorption of the nitrogen peroxide m the gases that are drawn from the chamber at the end of the ries, is known as the "Gay-Lussac Tower," Fig. 112, T. This nsists of a square leaden tower filled with fragments of coke, d down which there is caused to slowly percolate, a stream of ld strong sulphuric acid, the acid being evenly spread over the ıss of coke by a special distributing arrangement. The nitrogen roxide is absorbed by the acid, with the formation of nitrolphonic acid, $SO_2(HO)(NO_2)$. In order to make use of the sorbed nitroxygen compound, the acid which flows from the ıy-Lussac tower is pumped to the top of another very similar wer, situated between the "burners" and the first of the chamrs, and known as the "Glover Tower," G. The hot gases from e burners, consisting of sulphur dioxide, nitrogen, and oxygen, gether with the small quantities of nitrogen peroxide from the tre pots, are made to pass up this tower on their way to the first amber, and meeting with the descending stream of nitro-sulıonic acid as it percolates through the mass of coke with which e tower is filled, denitrification of the latter takes place, thus—

$$2SO_2(HO)(NO_2) + SO_2 + 2H_2O = 2NO + 3SO_2(HO)(HO),$$
$$\text{or } 3H_2SO_4.$$

The nitric oxide thus evolved, in presence of the atmospheric ygen, is converted into nitrogen peroxide, and swept along with e other gases into the chambers.

In practice, it is usual to deliver down the Glover tower, besides e nitro-sulphonic acid, a quantity of "chamber acid" from a parate tank. The effect of the heated gases upon this dilute id, is to remove a portion of the water from it, thereby effecting partial concentration, and furnishing the water demanded by e above equation. It will be seen, therefore, that there is a rubber tower at each end of the series of chambers, the Gay-Lussac" at the exit, where nitrogen peroxide is absorbed; ıd the "Glover" at the commencement, where the dissolved trogen compound is again liberated and returned to the ıambers.

(4.) The chambers are made of sheet lead, connected together by fusing the edges by means of an oxyhydrogen flame, without the intervention of solder, as the presence of another metal gives rise to the rapid corrosion of the lead on account of galvanic action being set up; this method of joining the lead is known as *autogenous soldering*. The enormous leaden chamber is supported in a framework of wood, to which the lead is secured by bands of the same metal, and the whole is usually supported on iron or brick pillars.

The general arrangement of a modern sulphuric acid works is seen in Fig. 112. The gases from the double row of pyrites burners B, are led through the Glover tower G, where they effect the denitrification of the nitro-sulphonic acid, as already explained. From this tower they are delivered into the series of chambers, where they meet with the necessary supply of steam. The acid collects upon the floor of the chambers, and samples are constantly drawn off by means of an arrangement known as *drip pipe*, which, acting in a manner similar to a rain gauge, indicates the progress of the processes going on within. The gases after being drawn through the entire series of chambers, by means of the draught caused by the tall chimney, are finally passed up the Gay-Lussac tower T, where all the nitrogen peroxide is absorbed, and returned to the chambers through the intervention of the Glover tower G, as above described.

The acid which collects in the chambers, is usually not permitted to reach a higher specific gravity than about 1.6, when it contains about 68 per cent. of sulphuric acid; for if the strength be allowed to exceed this, the acid not only begins to dissolve the nitrogen peroxide in the chamber, but exerts a corrosive action upon the lead of which the chamber is constructed. It is therefore withdrawn, and the first stage in the further concentration is effected either by the action of the Glover tower, or by evaporation in shallow leaden pans.

In order to bring up the strength of the acid to that of "oil of vitriol," that is, to about 98 per cent., the acid from the Glover tower, or the leaden pans, is heated in either glass or platinum stills.

Sulphuric acid, unless specially purified, is liable to contain a number of impurities, such as lead sulphate, derived from the action of the acid upon the chamber; arsenic, from the pyrites employed; oxides of nitrogen, and sulphur dioxide. From most of the impurities, except the arsenic, the acid may be purified by the addition of ammonium sulphate, and subsequent redistillation—

$$(NH_4)_2SO_4 + 2SO_2(HO)(NO_2) = 3H_2SO_4 + 2H_2O + 2N_2.$$

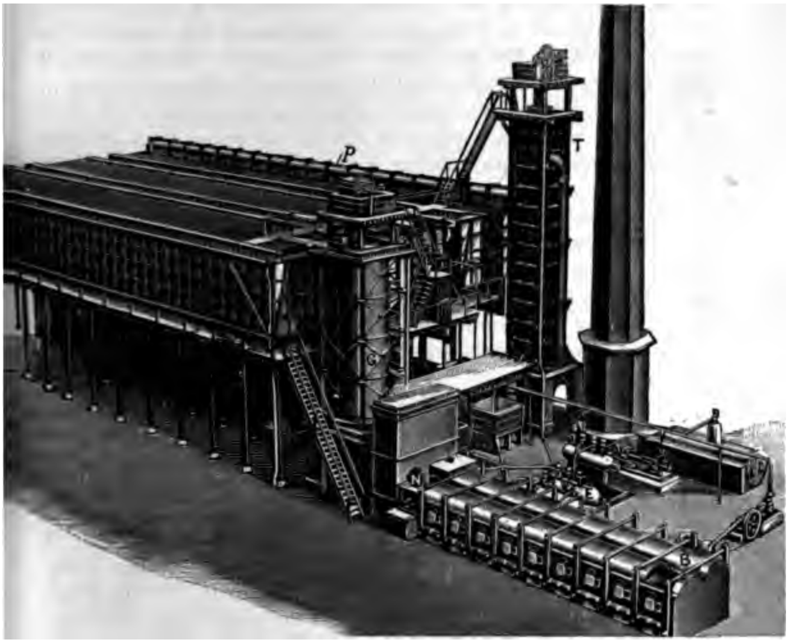


FIG. 112.

B.—Double row of pyrites burners, placed back to back: one being shown open.
N.—Hearth where the nitre pots are placed: one shown as open.
G.—Glover Tower, with two tanks at top: one for the nitro-sulphuric acid derived from the Gay-Lussac tower, the other for the "chamber acid." These acids are forced up from the leaden vessels E, called "eggs."
C.—Leaden chamber, of which there are three shown in the figure.
*P.*—Pipe conveying the gases from the third chamber to the Gay-Lussac tower.
T.—Gay-Lussac Tower. The tanks at the top of this and the Glover tower are enclosed in wooden sheds.

Arsenic may be removed by boiling the acid with hydrochloric acid or sodium chloride, when it passes away as arsenious chloride.

**Properties.**—Sulphuric acid is a perfectly colourless, heavy, oily liquid. The acid obtained by distillation, always contains about 2 per cent. of water; stronger than this it cannot be prepared by evaporation or distillation. When, however, acid of this strength is cooled to 0°, colourless crystals of pure sulphuric acid, containing 100 per cent. $H_2SO_4$, are deposited. The crystals melt at 10.5°, and remain liquid at temperatures much below this point. The specific gravity of the pure acid is 1.854 at 0°. When boiled, it gives off sulphur trioxide until the amount of water in it rises to 1.5 per cent., when it distils unchanged at a temperature of 338°.

Sulphuric acid has a powerful affinity for water, and absorbs moisture from the atmosphere with great readiness. On this account it constitutes one of the most valuable desiccating agents, and is constantly made use of for depriving gases, upon which it exerts no chemical action, of aqueous vapour. Owing to its strong affinity for water, it decomposes many organic substances containing hydrogen and oxygen, withdrawing from the compounds these elements in the proportion to yield water: its action upon formic acid, oxalic acid (see Carbon Monoxide), and alcohol (see Ethylene) are examples of this action.

When the acid is poured upon such substances as wood or sugar, the elements composing water are withdrawn, and the carbon is liberated, with the result that the compounds are blackened or charred.

When sulphuric acid is mixed with water, considerable heat is disengaged, the temperature often rising to the boiling-point of water, and at the same time a diminution in volume takes place. The maximum contraction is obtained upon mixing the materials in the proportion of one molecule of acid to two molecules of water. The diminution in volume in this case amounts to 8 per cent., and the composition of the acid produced, corresponds to the formula $H_2SO_4,2H_2O$.

Sulphuric acid combines with water in various proportions, forming a number of hydrates, and cryohydrates, of a more or less definite character. The best known hydrates are those represented by the formulæ $H_2SO_4,H_2O$ and $H_2SO_4,2H_2O$. These compounds may be regarded as respectively tetrabasic and hexabasic sulphuric acid, and their relation to the ordinary dibasic acid may be expressed by the following formulæ—

$$\begin{array}{llll} H_2SO_4 & . \quad . \quad . & \text{or} & SO_2(HO)_2. \\ H_4SO_5 & \text{or } H_2SO_4,H_2O & ,, & SO(HO)_4. \\ H_6SO_6 & ,, \; H_2SO_4,2H_2O & ,, & S(HO)_6. \end{array}$$

Salts of each of these acids are known—

| | | |
|---|---|---|
| Hydrogen potassium sulphate | $HKSO_4$ | Derived from $H_2SO_4$. |
| Normal potassium sulphate | $K_2SO_4$ | |
| Barium sulphate | $BaSO_4$ | |
| Tetrabasic lead sulphate | $Pb_2SO_5$ | ,, ,, $H_4SO_5$. |
| Hexabasic mercuric sulphate (Turpeth mineral) | $Hg_3SO_6$ | ,, ,, $H_6SO_6$. |

Most sulphates are soluble in water: those of lead, calcium, and trontium are only very sparingly soluble, whilst barium sulphate is nsoluble both in water and acids. The presence of sulphuric acid r a sulphate, may therefore be readily detected by the addition of soluble barium salt, which causes the immediate precipitation of hite barium sulphate, insoluble in hydrochloric acid.

## YROSULPHURIC ACID (*Nordhausen Acid; Fuming Sulphuric Acid*).

Formula, $H_2S_2O_7$ or $\left.\begin{matrix}HO\cdot SO_2\\ HO\cdot SO_2\end{matrix}\right\}O$.

**Modes of Formation.**—(1.) This acid may be obtained by dissolving sulphur trioxide in ordinary sulphuric acid—

$$H_2SO_4 + SO_3 = H_2S_2O_7.$$

n cooling the solution to 0°, the pyrosulphuric acid separates out n the form of large colourless crystals.

(2.) Pyrosulphuric acid is manufactured by the distillation of errous sulphate in clay retorts, mounted in series in a large 'galley" furnace. The first action of heat upon crystallised ferrous ulphate (green vitriol) is to expel six molecules of water of crystalisation, leaving the salt of the composition $FeSO_4,H_2O$. When his substance is further heated it is decomposed finally into ferric xide, with the formation of sulphur trioxide, water, and sulphur lioxide, thus—

$$2FeSO_4,H_2O = Fe_2O_3 + SO_3 + SO_2 + 2H_2O.$$

The decomposition takes place in two stages, the sulphur dioxide nd water being evolved in the first part of the process with the ormation of ferric sulphate, which is afterwards broken up in the nanner shown in the following equation—

(1.) $6FeSO_4,H_2O = Fe_2(SO_4)_3 + 2Fe_2O_3 + 3SO_2 + 6H_2O.$
(2.) $Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3.$

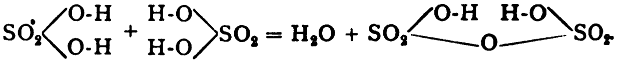
The sulphur trioxide is condensed in receivers, containing either a small quantity of water, or a charge of sulphuric acid.

(3.) Pyrosulphuric acid may also be obtained by decomposing sodium pyrosulphate ($Na_2S_2O_7$), either by heating it to a high temperature (see Sulphur Trioxide, page 383), or by acting upon it with sulphuric acid, thus—

$$Na_2S_2O_7 + H_2SO_4 = 2HNaSO_4 + SO_3.$$

The sulphur trioxide obtained, is dissolved in sulphuric acid, as in the former methods; and the hydrogen sodium sulphate, when gently heated to about 300°, is reconverted into pyrosulphate by the loss of a molecule of water (page 383).

**Properties.**—Pyrosulphuric acid is a colourless, strongly fuming liquid, having a specific gravity of 1.88. When cooled, it solidifies to a crystalline mass, which melts at 35°. The compound may be regarded as consisting of one molecule of sulphuric acid *plus* a molecule of sulphur trioxide, $H_2SO_4,SO_3$; or, as being derived from two molecules of sulphuric acid, by the withdrawal of one molecule of water, thus—



$$SO_2\left\langle\begin{matrix}O\text{-}H\\O\text{-}H\end{matrix}\right. + \left.\begin{matrix}H\text{-}O\\H\text{-}O\end{matrix}\right\rangle SO_2 = H_2O + SO_2\begin{matrix}O\text{-}H \quad H\text{-}O\\ \diagup\!\!-\!\!-\!\!-O\!-\!\!-\!\!-\!\!\diagdown\end{matrix}SO_2.$$

Pyrosulphuric acid forms a stable series of salts, of which the sodium compound already mentioned is a typical example. These salts are sometimes spoken of as the *disulphates*, and are analogous to the dichromates (*q.v.*).

Two other definite compounds of sulphur trioxide and sulphuric acid are known to exist, both of which are fuming acids. The composition of these substances is expressed by the formulæ—

$$H_2SO_4,3SO_3, \text{ or } H_2S_4O_{13}; \text{ and } 3H_2SO_4,SO_3, \text{ or } H_6S_4O_{15}.$$

## THIOSULPHURIC ACID.

Formula, $H_2S_2O_3$.

This acid has never been obtained in the free state, as it decomposes almost as soon as liberated from its salts, into sulphur dioxide and water, with precipitation of sulphur—

$$H_2S_2O_3 = SO_2 + H_2O + S.$$

The thiosulphates, however, are stable and important salts, the sodium salt being largely used in photography under the name of ***hyposulphite of soda***, or "hypo."

**Modes of Formation of Thiosulphates.**—(1.) These salts may be obtained by digesting flowers of sulphur with solutions of the sulphites, thus—

$$Na_2SO_3 + S = Na_2S_2O_3.$$

(2.) Sodium thiosulphate is also formed, when sulphur dioxide is passed into a solution of sodium sulphide. The reaction may be regarded as taking place in three steps, in which sodium sulphite and sulphuretted hydrogen are the first products. The latter compound is then acted upon by sulphur dioxide with the precipitation of sulphur, thus—

$$SO_2 + H_2O + Na_2S = Na_2SO_3 + H_2S.$$
$$SO_2 + 2H_2S = 2H_2O + 3S.$$

And the sulphur reacts with the already formed sulphite, as indicated in the equation given above.

(3.) When sulphur is boiled with sodium hydroxide, or with milk of lime, mixtures of sulphides and thiosulphates are obtained in both cases—

$$6NaHO + 4S = Na_2S_2O_3 + 2Na_2S + 3H_2O.$$
$$3Ca(HO)_2 + 12S = CaS_2O_3 + 2CaS_5 + 3H_2O.$$

The sodium sulphide can be converted into thiosulphate by the reactions given above. Calcium pentasulphide, on exposure to air, absorbs oxygen and forms a further quantity of thiosulphate with precipitation of sulphur—

$$CaS_5 + 3O = 3S + CaS_2O_3.$$

The thiosulphates are decomposed by most acids, with the liberation of sulphur dioxide, and precipitation of sulphur. They show a great tendency to form double salts, many of which are soluble in water; thus sodium thiosulphate, in contact with either silver chloride, bromide, or iodide, forms the soluble double sodium-silver thiosulphate, $NaAgS_2O_3$—

$$Na_2S_2O_3 + AgCl = NaCl + NaAgS_2O_3.$$

The employment of sodium thiosulphate in photography, for "fixing" negatives or silver prints, depends upon this property.

Thiosulphuric acid may be regarded as being derived from sulphuric acid by the replacement of one of the (HO) or hydroxyl groups, by an equivalent of (HS) or hydrosulphyl—

$$\left.\begin{matrix}HO\\HO\end{matrix}\right\}SO_2. \quad \left.\begin{matrix}HS\\HO\end{matrix}\right\}SO_2.$$

**Dithionic Acid,** $H_2S_2O_6$ or $\left.\begin{matrix}HO{\cdot}SO_2\\HO{\cdot}SO_2\end{matrix}\right\}$.—This compound is prepared, by passing a stream of sulphur dioxide through water in which manganese dioxide is suspended, whereby manganese dithionate is formed; while at the same time a portion of the salt is acted upon by manganese dioxide, and converted into manganous sulphate, thus—

$$2SO_2 + MnO_2 = MnS_2O_6.$$
$$MnS_2O_6 + MnO_2 = 2MnSO_4.$$

On the addition of barium hydroxide to the solution, barium dithionate, barium sulphate, and manganous hydrate are formed—

$$MnS_2O_6 + Ba(HO)_2 = BaS_2O_6 + Mn(HO)_2.$$

Barium dithionate, being soluble, is separated by filtration, and upon evaporation separates out in crystals of the composition $BaS_2O_6,2H_2O$.

Upon the addition of dilute sulphuric acid in amount demanded by the equation

$$BaS_2O_6 + H_2SO_4 = BaSO_4 + H_2S_2O_6,$$

the acid itself is obtained. The solution may be concentrated in vacuo until it reaches a specific gravity of 1.347. Further concentration results in its decomposition into sulphuric acid and sulphur dioxide—

$$H_2S_2O_6 = SO_2 + H_2SO_4.$$

Dithionic acid forms well-defined crystalline salts, which on heating, decompose into sulphates with evolution of sulphur dioxide.

Dithionic acid was formerly called *hyposulphuric* acid, and its salts are still sometimes referred to as *hyposulphates*.

**Trithionic Acid,** $H_2S_3O_6$ or $\left.\begin{matrix}HO{\cdot}SO_2\\HO{\cdot}SO_2\end{matrix}\right\}S$.—The potassium salt of this acid may be obtained, by passing sulphur dioxide through a strong solution of potassium thiosulphate—

$$3SO_2 + 2K_2S_2O_3 = S + 2K_2S_3O_6.$$

It is also formed when a solution of potassium silver thiosulphate is boiled—

$$\begin{matrix}\left.\begin{matrix}KO\\AgS\end{matrix}\right\}SO_2\\\left.\begin{matrix}AgS\\KO\end{matrix}\right\}SO_2\end{matrix} = Ag_2S + \left.\begin{matrix}KO{\cdot}SO_2\\KO{\cdot}SO_2\end{matrix}\right\}S.$$

The sodium salt may be obtained, by the addition of iodine to a mixture of sodium sulphite and thiosulphate—

$$\left.\begin{matrix}\mathrm{NaO}\\ \mathrm{NaS}\end{matrix}\right\}\mathrm{SO_2} + \mathrm{Na_2SO_3} + \mathrm{I_2} = 2\mathrm{NaI} + \left.\begin{matrix}\mathrm{NaO{\cdot}SO_2}\\ \mathrm{NaO{\cdot}SO_2}\end{matrix}\right\}\mathrm{S}.$$

The acid itself is obtained by the addition of fluosilicic acid to a solution of the potassium salt, when insoluble potassium fluosilicate is precipitated.

Both the acid itself, and its salts, are readily decomposed into sulphur dioxide, sulphur, and either sulphuric acid or a sulphate, thus—

$$\mathrm{K_2S_3O_6} = \mathrm{K_2SO_4} + \mathrm{SO_2} + \mathrm{S}.$$

When acted upon by sodium amalgam, sodium trithionate is converted back again into its generators, sodium sulphite and thiosulphate, thus—

$$\left.\begin{matrix}\mathrm{NaO{\cdot}SO_2}\\ \mathrm{NaO{\cdot}SO_2}\end{matrix}\right\}\mathrm{S} + \mathrm{Na_2} = \mathrm{Na_2SO_3} + \left.\begin{matrix}\mathrm{NaO}\\ \mathrm{NaS}\end{matrix}\right\}\mathrm{SO_2}.$$

**Tetrathionic Acid,** $\mathrm{H_2S_4O_6}$ or $\left.\begin{matrix}\mathrm{HO{\cdot}SO_2}\\ \mathrm{HO{\cdot}SO_2}\end{matrix}\right\}\mathrm{S_2}$.—The sodium salt is obtained by the action of iodine upon sodium thiosulphate—

$$2\mathrm{NaS{\cdot}NaO{\cdot}SO_2} + \mathrm{I_2} = 2\mathrm{NaI} + \left.\begin{matrix}\mathrm{NaO{\cdot}SO_2}\\ \mathrm{NaO{\cdot}SO_2}\end{matrix}\right\}\mathrm{S_2}.$$

The barium salt, from which the acid itself is most readily obtained, is prepared by the gradual addition of iodine to barium thiosulphate in water—

$$2\mathrm{BaS_2O_3} + \mathrm{I_2} = \mathrm{BaI_2} + \mathrm{BaS_4O_6}.$$

The barium tetrathionate is separated by the addition of alcohol, which dissolves the iodide and excess of iodine, leaving the tetrathionate. By the addition of dilute sulphuric acid to an aqueous solution of this salt, in amount demanded by the equation—

$$\mathrm{BaS_4O_6} + \mathrm{H_2SO_4} = \mathrm{H_2S_4O_6} + \mathrm{BaSO_4},$$

a dilute aqueous solution of the acid may be obtained. The dilute acid may be boiled without decomposition; but when concentrated, it readily passes into sulphuric acid, sulphur dioxide, and sulphur.

Sodium amalgam decomposes the sodium salt into two molecules of thiosulphate, reversing the reaction by which it is produced.

**Pentathionic Acid,** $\mathrm{H_2S_5O_6}$ or $\left.\begin{matrix}\mathrm{HO{\cdot}SO_2}\\ \mathrm{HO{\cdot}SO_2}\end{matrix}\right\}\mathrm{S_3}$.—This acid is prepared by passing sulphuretted hydrogen into a strong aqueous solution of sulphur dioxide—

$$5\mathrm{SO_2} + 5\mathrm{H_2S} = \mathrm{H_2S_5O_6} + 5\mathrm{S} + 4\mathrm{H_2O}.$$

or—

$$5\mathrm{H_2SO_3} + 5\mathrm{H_2S} = \mathrm{H_2S_5O_6} + 5\mathrm{S} + 9\mathrm{H_2O}.$$

The solution contains, however, more or less of the other thionic acids, but as the passage of sulphuretted hydrogen is continued, these are gradually decomposed, and ultimately the pentathionic acid also, so that the final products of the action of excess of this gas will be sulphur and water—

$$H_2S_5O_6 + 5H_2S = 6H_2O + 10S.$$

The solution obtained by the first action, may be concentrated by cautious evaporation in vacuo, until a specific gravity of 1.46 is obtained, when on partial saturation with potassium hydroxide and filtration, a solution is obtained which on spontaneous evaporation deposits crystals of potassium pentathionate, having the composition $K_2S_5O_6,3H_2O$. On heating, the salt splits up into potassium sulphate, sulphur dioxide, and sulphur.

## OXYCHLORIDES OF SULPHUR.

Four of these compounds are known, all of which may be regarded as being derived from the oxyacids by the replacement of hydroxyl (HO) by its equivalent of chlorine.

| | | | | | |
|---|---|---|---|---|---|
| 1. | Thionyl chloride, or<br>*Sulphurous chloride* | $\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}SO$ | corresponding oxyacid | $\left.\begin{matrix}HO\\HO\end{matrix}\right\}SO,$ | sulphurous acid. |
| 2. | Sulphuryl chloride, or<br>*Sulphuric chloride* | $\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}SO_2$ | ,, ,, | $\left.\begin{matrix}HO\\HO\end{matrix}\right\}SO_2,$ | sulphuric acid. |
| 3. | Sulphuric chlorhydrate, or<br>*Chlorosulphonic acid* | $\left.\begin{matrix}Cl\\HO\end{matrix}\right\}SO_2$ | ,, ,, | | |
| 4. | Disulphuryl chloride, or<br>*Pyrosulphuric chloride* | $\left.\begin{matrix}Cl{\cdot}SO_2\\Cl{\cdot}SO_2\end{matrix}\right\}O$ | ,, ,, | $\left.\begin{matrix}HO{\cdot}SO_2\\HO{\cdot}SO_2\end{matrix}\right\}O,$ | pyrosulphuric acid. |

**Thionyl Chloride,** $SOCl_2$, molecular weight = 118.76, is obtained by the action of phosphorus pentachloride upon sodium sulphite—

$$SO(NaO)_2 + 2PCl_5 = SOCl_2 + 2POCl_3 + 2NaCl.$$

It is also obtained when dry sulphur dioxide is passed over phosphorus pentachloride—

$$SO_2 + PCl_5 = SOCl_2 + POCl_3.$$

**Properties.**—Thionyl chloride is a colourless and highly refractive liquid, which fumes in moist air, and has a pungent unpleasant smell. It boils at 78°, and is at once decomposed by water, into its corresponding oxyacid with formation of hydrochloric acid—

$$SOCl_2 + 2H_2O = H_2SO_3 + HCl.$$

**Sulphuryl Chloride,** $SO_2Cl_2$; molecular weight = 134.72. This compound (sometimes known as *chlorosulphuric acid*) can be obtained by the direct union of chlorine and sulphur dioxide, under the prolonged influence of bright sunlight—

$$SO_2 + Cl_2 = SO_2Cl_2.$$

It is also formed by the action of heat upon sulphuric chlorhydrate.

This substance, on being simply heated to 180° in sealed tubes for a few hours, breaks up into sulphuryl chloride and sulphuric acid—

$$2\left.\begin{matrix}HO\\Cl\end{matrix}\right\}SO_2=\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}SO_2+\left.\begin{matrix}HO\\HO\end{matrix}\right\}SO_2.$$

**Properties.**—Sulphuryl chloride is a colourless liquid, which fumes in moist air, and has a specific gravity of 1.66. It boils at 70°, and is decomposed by water with formation of sulphuric acid and hydrochloric acid—

$$\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}SO_2+2H_2O=2HCl+\left.\begin{matrix}HO\\HO\end{matrix}\right\}SO_2.$$

**Sulphuric Chlorhydrate,** $SO_2Cl(HO)$. This compound is the first product of the replacement of the (HO) groups in sulphuric acid by chlorine, and is formed by the direct combination of sulphur trioxide and hydrochloric acid—

$$SO_3+HCl=HClSO_3\text{ or }SO_2Cl(HO).$$

It may be obtained by distilling sulphuric acid with phosphorus oxychloride

$$2\left.\begin{matrix}HO\\HO\end{matrix}\right\}SO_2+POCl_3=2\left.\begin{matrix}HO\\Cl\end{matrix}\right\}SO_2+HCl+HPO_3.$$

Or by passing dry gaseous hydrochloric acid into melted pyrosulphuric acid—

$$H_2S_2O_7+2HCl=H_2O+2HClSO_3.$$

**Properties.**—Sulphuric chlorhydrate is a colourless fuming liquid, having a specific gravity of 1.76, and boiling at 149°–151°, with partial dissociation into its generators, sulphur trioxide and hydrochloric acid. In contact with water it is decomposed with considerable violence, with formation of sulphuric and hydrochloric acids—

$$\left.\begin{matrix}HO\\Cl\end{matrix}\right\}SO_2+H_2O=HCl+\left.\begin{matrix}HO\\HO\end{matrix}\right\}SO_2.$$

**Disulphuryl Chloride** (*pyrosulphuric chloride*), $\left.\begin{matrix}ClSO_2\\ClSO_2\end{matrix}\right\}O$ or $S_2O_5Cl_2$. This substance is obtained by the action of sulphur trioxide, or sulphuric chlorhydrate, upon phosphorus pentachloride—

$$2SO_3+PCl_5=POCl_3+S_2O_5Cl_2.$$
$$2SO_2Cl(HO)+PCl_5=POCl_3+2HCl+S_2O_5Cl_2.$$

It is also produced by the action of sulphur trioxide upon sulphur dichloride—

$$5SO_3+S_2Cl_2=S_2O_5Cl_2+5SO_2.$$

Or by the action of sulphur trioxide upon sulphuric chloride—

$$\left.\begin{matrix}Cl\\Cl\end{matrix}\right\}SO_2+SO_3=\left.\begin{matrix}ClSO_2\\ClSO_2\end{matrix}\right\}O.$$

**Properties.**—Pyrosulphuric chloride is a heavy, oily, fuming liquid, resembling pyrosulphuric acid in appearance. It has a specific gravity of 1.819, and boils at 146°. When mixed with water it slowly decomposes into sulphuric and hydrochloric acids, showing a marked difference in this respect from sulphuric chlorhydrate—

$$S_2O_5Cl_2 + 3H_2O = 2H_2SO_4 + 2HCl$$

## CARBON DISULPHIDE.

Formula, $CS_2$. Molecular weight = 76. Vapour density = 38.

**History.**—This compound was accidentally produced by Lampadius (1796) when heating a mixture of charcoal and pyrites.

**Mode of Formation.**—Carbon disulphide is prepared by passing the vapour of sulphur over red-hot charcoal, when the two elements unite and form the volatile product, which is condensed in vessels surrounded with cold water—

$$C + S_2 = CS_2.$$

The product is always contaminated with free sulphur, which volatilises, and is also accompanied by considerable quantities of sulphuretted hydrogen, formed by the action of sulphur upon the hydrogen contained in the charcoal.

When carbon disulphide is prepared on a manufacturing scale, the charcoal is heated in a vertical cast-iron or earthenware retort, C, Fig. 113, having an elliptical section, and provided with three openings. The retort is built into a suitable furnace, whereby it can be uniformly heated to redness. A quantity of sulphur, contained in the pot S, kept liquid by the heat of the furnace, is allowed to enter at intervals through the pipe B. As the vapour comes in contact with the red-hot charcoal, combination ensues, and the carbon disulphide escapes through the pipe D, which is inclined to the retort so as to allow condensed sulphur to run back. Sulphur which escapes condensation in this pipe, collects, for the most part, in the vessel E, which is closed by water seals as seen in the figure. The volatile compounds are then passed through a Liebig's condenser about 30 ft. long, and the crude disulphide so condensed is collected in a receiver. Any vapour of carbon disulphide which is carried on by the sulphuretted hydrogen, is absorbed by passing the gas through a scrubber containing oil; and finally the tted hydrogen is absorbed in a lime purifier, similar to nployed for the purification of coal gas. The ashes are wn from the retort through the wide tube B; and the arcoal is introduced through the opening A. In order to the escape of the unpleasant and injurious vapours from g the addition of fresh charcoal, the opening A′ is put into iication with the chimney of the furnace. The sulphur lows back into the retort from D, is conveyed by means ipe *f*, nearly to the bottom of the mass of heated char- that its vapour shall once made to pass over the

crude product is purified illation, and subsequent n with mercury.

**erties.** — Carbon disul- a colourless, mobile, and refracting liquid. When pure it possesses a sweet- not unpleasant, ethereal ut as usually met with the decidedly fœtid. ecific gravity at 0° is 1.292, oils at 46°. The vapour n disulphide has a very ting-point (see page 291). It burns with a blue flame, vhen fed with oxygen, emits a dazzling blue light. When disulphide vapour is mixed with three times its volume en, and a light applied, the mixture explodes with ; the products of the combustion being carbon dioxide hur dioxide—

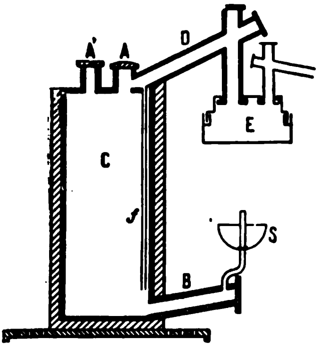


FIG. 113.

$$CS_2 + 3O_2 = CO_2 + 2SO_2.$$

apour of carbon disulphide, when constantly inhaled in iantities, has an injurious effect upon the health, and if l in large quantities is a powerful poison.

heated to a bright red heat, carbon disulphide vapour is sed into its constituent elements: on this account, in the ture of this compound, care is taken that the temperature rise too high.

apour of carbon disulphide is decomposed by potassium, which, when heated, burns in the vapour, forming potassium sulphide, and liberating carbon—

$$CS_2 + 2K_2 = C + 2K_2S.$$

When passed over heated slaked lime, carbon disulphide vapour is converted into carbon dioxide and sulphuretted hydrogen—

$$CS_2 + 2CaH_2O_2 = 2CaO + CO_2 + 2H_2S.$$

This reaction is made use of for converting the carbon disulphide, which is always present in coal gas, into the two easily removed substances, carbon dioxide and sulphuretted hydrogen.

When a mixture of carbon disulphide vapour and sulphuretted hydrogen, is passed over heated copper, marsh gas is formed—

$$4Cu + CS_2 + 2H_2S = CH_4 + 4CuS.$$

Carbon disulphide is soluble to a minute extent in water; 1 volume of water dissolves .001 volume of this liquid, and the solution possesses the taste and the smell of the disulphide. It mixes in all proportions with alcohol, ether, the hydrocarbons of the benzene family, and most essential oils. It also dissolves sulphur, phosphorus, iodine, bromine, caoutchouc, and most fats; and is largely used in the arts, both as a solvent for caoutchouc, and in extracting essential oils, spices, and perfumes.

**Thiocarbonic Acid.**—Carbon disulphide is the sulphur analogue of carbon dioxide, $CS_2$; $CO_2$. Like the oxygen compound, it forms a feeble acid, which has received the name thiocarbonic acid, $H_2CS_3$; carbonic acid, $H_2CO_3$.

The thiocarbonates are produced by reactions analogous to those by which carbonates are formed. Thus, when carbon disulphide is brought into contact with potassium sulphide, potassium thiocarbonate is obtained—

$$CS_2 + K_2S = K_2CS_3,$$

which may be compared with the action of carbon dioxide upon potassium oxide—

$$CO_2 + K_2O = K_2CO_3.$$

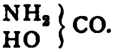
Thiocarbonates are likewise formed by the action of carbon disulphide upon metallic hydroxides—

$$3CS_2 + 6KHO = 2K_2CS_3 + K_2CO_3 + 3H_2O.$$

The acid itself is obtained as a yellow oil, having an unpleasant odour, by the decomposition of a thiocarbonate by dilute hydrochloric acid.

A large number of compounds are known, in which divalent sulphur replaces oxygen, and which therefore stand in the same relation to the oxygen compounds, as thiocarbonic acid stands to carbonic acid; for example—

Thiocarbamic acid, $CS_2NH_3$, or $\left.\begin{matrix}NH_2\\HS\end{matrix}\right\}CS$;

Carbamic acid, $CO_2NH_3$, or  $\left.\begin{matrix}NH_2\\HO\end{matrix}\right\}CO$.

**Other Compounds of Carbon and Sulphur.**—When carbon disulphide is exposed to the influence of light, there is gradually formed upon the glass vessel containing it, a brown deposit, which is believed to be carbon monosulphide, CS; the sulphur analogue of carbon monoxide. When electric sparks from carbon poles are passed through the vapour of carbon disulphide, or when the electric arc is produced in the vapour, an offensive-smelling liquid is obtained, which exerts a most irritating and tear-producing effect upon the eyes. This liquid has been shown to have the composition $C_3S_2$.*

## SELENIUM.

Symbol, Se. Atomic weight = 78.87. Molecular weight = 157.74.

**History.**—This element was discovered by Berzelius (1817), who gave it the name selenium (signifying the moon) on account of its close analogy with the previously discovered element tellurium (signifying the earth).

**Occurrence.**—Selenium is occasionally met with associated with native sulphur, probably as a selenide of sulphur. In a few minerals of considerable rarity, selenium is met with in the form of selenides of such metals as mercury, lead, silver. It occurs in very small quantities in a large number of metallic sulphides.

**Modes of Formation.**—(1.) When pyrites containing selenium is employed in the manufacture of sulphuric acid, the selenium is oxidised by the atmospheric oxygen into selenium dioxide, which is carried forward with the sulphur dioxide. Selenium dioxide, being a solid substance, is partly deposited in the flues, and in the Glover tower, and partly carried forward into the chambers, where it forms a red-coloured deposit. To obtain the selenium, either the flue dust or the chamber deposit, is first boiled with dilute sulphuric acid, and either nitric acid or potassium chlorate added, in order to oxidise it completely into selenic acid, $H_2SeO_4$. The solution is then boiled with strong hydrochloric acid, whereby it is reduced to selenious acid, $H_2SeO_3$, when a stream of sulphur dioxide is passed through it which precipitates the selenium as a red powder—

$$H_2SeO_3 + 2SO_2 + H_2O = Se + 2H_2SO_4.$$

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* Von Lengyel, 1894.

(2.) A second method for the preparation of selenium from the chamber deposit, consists in digesting the substance with potassium cyanide, whereby it is converted into soluble potassium selenocyanide, SeK(CN). On the addition of hydrochloric acid to this solution, the element is precipitated as a red amorphous powder, and hydrocyanic acid and potassium chloride go into solution—

$$SeK(CN) + HCl = Se + KCl + H(CN).$$

**Properties.**—Selenium is known in various allotropic modifications.

1. *Soluble in carbon disulphide.*—*α.* Brick-red amorphous powder, obtained by precipitation with acids, or reduction of selenious acid, in the cold, by sulphur dioxide.

*β.* Black crystalline powder, obtained by reduction of hot selenious acid by sulphur dioxide.

*γ.* Dark red translucent monoclinic crystals, specific gravity 4.5, deposited from solution in carbon disulphide.

*δ.* Black, shining, brittle amorphous mass, having a conchoidal fracture, and a specific gravity of 4.3, obtained by rapidly cooling melted selenium.

2. *Insoluble in carbon disulphide.*—Black, metallic-looking crystalline mass, having a granular fracture. Obtained by quickly cooling melted selenium to 210° and keeping it for some time at that temperature, when the mass solidifies with rise of temperature to 217°. This insoluble variety, sometimes called *metallic* selenium, is also formed as a deposit of minute black crystals, when concentrated solutions of sodium or potassium selenide are exposed to the air.

This modification has a specific gravity of 4.5, and melts at 217°.

Selenium boils at 680°, forming a dark red vapour which condenses in the form of *flowers of selenium*, having a scarlet-red colour.

At high temperatures the vapour of selenium, like that of sulphur, becomes a true gas; thus at 1420°, the vapour density is found to be 81.5, approaching very closely to the normal density demanded by the molecule $Se_2$.

"Metallic" selenium conducts electricity, and the element exhibits the remarkable property of having its conductivity increased by light; the conductivity of selenium when exposed to diffused daylight being about twice as great as when in the dark. This alteration in the electrical resistance with varying intensities of light, is a property of selenium that was made use of, in the construction of an instrument known as the photophone, but it has not as yet been put to any practical use. When selenium is heated in the air, it burns with a blue flame, with the formation of selenium dioxide, and at the same time emits a powerful and characteristic smell resembling rotten horse-radish.

When selenium is heated in a tube, filled with an indifferent gas, it sublimes in the form of a red deposit; but when heated in hydrogen, the sublimate is in the form of black shining crystals. The formation of these crystals is due to the fact, that selenium combines with the hydrogen, and the hydrogen selenide is again decomposed by the heat.

**Hydrogen Selenide** (*selenuretted hydrogen*), $H_2Se$; molecular weight = 81. Hydrogen selenide is formed when selenium is heated in hydrogen.

This compound is also obtained, by the action of dilute hydrochloric or sulphuric acid, upon either potassium selenide or ferrous selenide—

$$FeSe + H_2SO_4 = FeSO_4 + H_2Se.$$

**Properties.**—Hydrogen selenide is a colourless gas, strongly resembling sulphuretted hydrogen, both in its smell, and in its chemical behaviour. It is readily soluble in water, and when passed through metallic solutions, precipitates insoluble selenides of most of the heavy metals. Hydrogen selenide burns with a blue flame, with the production of water and selenium dioxide. Its smell, although resembling that of its sulphur analogue, is more unpleasant, and its effects upon the system are more persistent and injurious. A single small bubble inhaled through the nostril, produces temporary paralysis of the olfactory nerves, accompanied by inflammation of the mucous membrane.

No compound of selenium corresponding to hydrogen disulphide is known.

## COMPOUNDS WITH HALOGENS.

**Diselenium Dichloride,** $Se_2Cl_2$, is obtained by passing chlorine over selenium, or by passing gaseous hydrochloric acid through a solution of selenium in nitric acid.

**Properties.**—Selenium chloride is a brown oily liquid, in which selenium itself is readily soluble, and from which the element is deposited in the form which is insoluble in carbon disulphide. It is slowly decomposed by water, thus—

$$2Se_2Cl_2 + 3H_2O = H_2SeO_3 + 3Se + 4HCl.$$

Corresponding bromine and iodine compounds are known, $Se_2Br_2$, and $Se_2I_2$.

**Selenium Tetrachloride,** $SeCl_4$, is prepared either by the action of chlorine upon selenium chloride—

$$Se_2Cl_2 + 3Cl_2 = 2SeCl_4,$$

or by heating a mixture of selenium dioxide and phosphorus pentachloride—

$$3SeO_2 + 3PCl_5 = 3SeCl_4 + P_2O_5 + POCl_3.$$

**Properties.**—Selenium tetrachloride is a white, crystalline, volatile compound; which may be sublimed without decomposition and without fusion. When the vapour is heated above 200°, it begins to dissociate into selenium and chlorine. It dissolves in water, with decomposition into hydrochloric and selenious acids—

$$SeCl_4 + 3H_2O = 4HCl + H_2SeO_3.$$

Corresponding bromine and iodine compounds are known, $SeBr_4$ and $SeI_4$.

## OXIDES AND OXYACIDS OF SELENIUM.

Only one oxide of selenium is known, namely, selenium dioxide, $SeO_2$, although a second oxide of unknown composition is believed to exist, and to constitute the peculiar smelling substance which is always formed when selenium is burnt in the air.

**Selenium Dioxide** is prepared by burning selenium in a stream of oxygen in a glass tube; the element burns in the gas with a blue flame, and the oxide condenses upon the distant portions of the tube, as a white crystalline deposit.

**Properties.**—Selenium dioxide crystallises in long white prisms, which when heated, readily sublime without passing through the state of liquidity. It dissolves in water and gives rise to selenious acid.

The following oxyacids of selenium are known—

Selenious acid, $H_2SeO_3$, corresponding to sulphurous acid, $H_2SO_3$.
Selenic acid, $H_2SeO_4$, corresponding to sulphuric acid, $H_2SO_4$.
Selenosulphuric acid, $\left.\begin{matrix}HO\\HSe\end{matrix}\right\}SO_2$, corresponding to thiosulphuric acid, $\left.\begin{matrix}HO\\HS\end{matrix}\right\}SO_2$.

**Selenious Acid,** $H_2SeO_3$, is obtained as a white crystalline compound, when the dioxide is dissolved in hot water, and the solution allowed to cool. The acid is dibasic, and forms both acid and normal selenites, corresponding to the sulphites: it also forms a series of so-called *superacid salts*, containing a molecule of the acid salt, combined with a molecule of acid, thus—

$$HKSeO_3, H_2SeO_3.$$

**Selenic Acid,** $H_2SeO_4$.—This acid is best prepared, by the addition of bromine to silver selenite suspended in water, when insoluble silver bromide is formed and selenic acid is left in solution—

$$Ag_2SeO_3 + H_2O + Br_2 = 2AgBr + H_2SeO_4.$$

The solution may be evaporated by heating, until it contains 94 per cent. of selenic acid, and still further evaporated in vacuo, until it reaches 97.4 per cent., when its specific gravity is 2.627. When heated to 280° it decomposes into selenium dioxide, water, and selenium.

**Properties.**—Selenic acid in its most concentrated condition, is a colourless, strongly acid liquid, which mixes with water with the development of considerable heat. It dissolves iron and zinc with evolution of hydrogen; and when heated, dissolves copper with formation of selenious acid.

The selenates closely resemble the sulphates. Barium selenate, like the sulphate, is quite insoluble in water, but differs from that compound in being converted by boiling hydrochloric acid into barium selenite, which is soluble.

Selenium also forms a compound with oxygen and chlorine, selenium oxychloride, or selenyl chloride, $SeOCl_2$, corresponding with thionyl chloride, $SOCl_2$.

## TELLURIUM.

Symbol, Te. Atomic weight,* 125 (?).

**Occurrence.**—In the free state, small quantities of this element have been found as crystals, consisting of almost pure tellurium. In combination it is met with in a few rare minerals, such as *tellurite* ($TeO_2$), and, more commonly, *tetradymite* ($Bi_2Te_3$). Some specimens of pyrites contain small quantities of this element, hence it is found in the deposit from the vitriol chambers, from which selenium is obtained.

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* Various numbers have been obtained, by different observers, for the atomic weight of tellurium. Some of these numbers are higher than the atomic weight of iodine, which would make it impossible to give to tellurium a position between antimony (atomic weight = 120) and iodine (atomic weight = 126.54) as demanded by the periodic law. Brauner, who has spent many years investigating this point, considers that hitherto *pure* tellurium has never been obtained.

**Mode of Formation.**—Tellurium is obtained from bismuth telluride, $Bi_2Te_3$, by fusion with an intimate mixture of sodium carbonate and carbon. The mass on treatment with water, yields a solution containing a mixture of sodium telluride and sodium sulphide, which on exposure to the air deposits tellurium as a grey powder. The element is purified by distillation in a stream of hydrogen.

**Properties.**—Tellurium is a bluish-white, silver-like solid, possessing metallic lustre. It conducts heat and electricity, although badly, and is very brittle. Its specific gravity is 6.26, and it melts at 452°. When melted tellurium is slowly cooled, it forms rhombohedral crystals. When heated in the air, it burns with a blue flame, and forms tellurium dioxide, $TeO_2$. When heated in a sealed tube with hydrogen, tellurium sublimes in the form of brilliant prismatic crystals.

**Hydrogen Telluride** (*Telluretted Hydrogen*), $H_2Te$.—When tellurium is heated in hydrogen, the elements combine, forming hydrogen telluride, which exhibits the same phenomenon as is shown by selenuretted hydrogen, of being decomposed by heat, and depositing the element as a crystalline sublimate.

Hydrogen telluride is obtained by the action of hydrochloric acid upon zinc telluride—

$$ZnTe + 2HCl = ZnCl_2 + H_2Te.$$

**Properties.**—Hydrogen telluride is a most offensive smelling, and highly poisonous gas. It behaves like sulphuretted hydrogen in precipitating metals from solutions. It is soluble in water, and the solution gradually absorbs oxygen and deposits tellurium.

### COMPOUNDS WITH THE HALOGENS.

Two chlorides of tellurium are known, namely, tellurium dichloride, $TeCl_2$, and tellurium tetrachloride, $TeCl_4$. It will be noticed that the composition of the dichloride is not analogous with the lower chloride of either selenium ($Se_2Cl_2$) or sulphur ($S_2Cl_2$).

Two bromides, $TeBr_2$ and $TeBr_4$, and corresponding iodides are known.

### OXIDES AND OXYACIDS OF TELLURIUM.

Two oxides of tellurium are known with certainty, namely, tellurium dioxide, $TeO_2$, and tellurium trioxide, $TeO_3$, which give rise respectively to the two acids, tellurous acid, $H_2TeO_3$, and telluric acid, $H_2TeO_4$.

**Tellurous Acid** is obtained, by pouring a solution of tellurium in nitric acid into an excess of water. The acid is precipitated as a white amorphous powder. When strongly heated, it is converted into the dioxide and water.

Tellurous acid, like sulphurous acid, is dibasic, and gives rise to both acid and normal salts: thus, with potassium it forms hydrogen potassium tellurite,

$HKTeO_3$, and dipotassium tellurite, $K_2TeO_3$. It also forms super-acid salts, such as—

| | |
|---|---|
| Quadracid potassium tellurite . . . | $HKTeO_3, H_2TeO_3$. |
| Potassium tetratellurite . . . . | $K_2TeO_3, 3TeO_2$. |

**Telluric Acid** is prepared by fusing either tellurium, or tellurium dioxide, with a mixture of potassium nitrate and carbonate—

$$Te_2 + K_2CO_3 + 2KNO_3 = 2K_2TeO_4 + N_2 + CO.$$

The fused mass, after solution in water, is mixed with a solution of barium chloride, which precipitates barium tellurate; this is then decomposed by the addition of the exact amount of sulphuric acid, and after filtration, the clear solution deposits crystals of telluric acid, $H_2TeO_4.2H_2O$. When these crystals are heated to 160°, the water is expelled, and the anhydrous acid in the form of a white powder is left. On strongly heating, telluric acid decomposes into water and tellurium trioxide, which at a higher temperature splits up into the dioxide and oxygen.

Like tellurous acid, telluric acid forms not only normal and acid salts, but a number of more complex superacid salts—

| | |
|---|---|
| Normal potassium tellurate . . . | $K_2TeO_4.5H_2O$. |
| Hydrogen potassium tellurate . . . | $HKTeO_4$. |
| Quadracid potassium tellurate . . . | $K_2TeO_4, H_2TeO_4, 3H_2O$. |
| Potassium tetratellurate . . . . | $K_2TeO_4.3H_2TeO_4, H_2O$. |

# CHAPTER III

## *THE ELEMENTS OF GROUP V. (FAMILY B.)*

| | | | |
|---|---|---|---|
| Nitrogen, N | 14.01 | Antimony, Sb | 119.6 |
| Phosphorus, P | 30.96 | Bismuth, Bi | 207.5 |
| Arsenic, As | 74.9 | | |

IN this family of elements we have a gradual transition from the non-metals to the metals. Nitrogen and phosphorus may be considered as typical non-metallic elements, both as regards their physical and chemical properties. The third member, arsenic, begins to exhibit metalline properties; its specific gravity is more than three times as high as that of phosphorus, and it possesses considerable metallic lustre: arsenic is called a *metalloid* on this account. Antimony is still more metallic in its character, possessing most of the physical attributes of a true metal, while in bismuth all non-metallic properties cease altogether to exist.

All these elements form more than one compound with oxygen, of which the following may be compared—

$$\begin{array}{lllll} N_2O_3; & (P_2O_3)_2; & (As_2O_3)_2; & Sb_2O_3; & Bi_2O_3. \\ N_2O_4; & P_2O_4; & — & Sb_2O_4; & Bi_2O_4. \\ N_2O_5; & P_2O_5; & As_2O_5; & Sb_2O_5; & Bi_2O_5. \end{array}$$

The oxides (which in the case of nitrogen and phosphorus are strongly acidic in their nature, combining with water to form acids) gradually become less and less acidic and more basic as the series is traversed.

Thus, nitrogen pentoxide, $N_2O_5$, unites violently with water to form nitric acid, which with bases yields nitrates. Antimony pentoxide is insoluble in water, and no antimonic acid has been isolated, although its salts, the antimonates, are known. The oxides of antimony, on the other hand, begin to exhibit basic properties, and unite with acids, forming salts in which the antimony functions as the base.

In the case of the last element, the acidic nature of the oxides is entirely lost; no bismuth compounds being known, corresponding to antimonates or arsenates, while these oxides unite with acids in the capacity of bases, giving rise to bismuth salts.

Four of the elements of this group unite with hydrogen, forming similarly constituted compounds, $NH_3$, $PH_3$, $AsH_3$, $SbH_3$.

The stability of these compounds gradually decreases as we pass from nitrogen to antimony. Antimony hydride has never been obtained free from other gases, while no similar bismuth compound is known. Ammonia is alkaline and strongly basic, and unites readily with acids to form ammonium salts. Phosphorus hydride has no alkaline character, and is only feebly basic. It combines, however, with the halogen acids to form phosphonium chloride, bromide, and iodide, $PH_4Cl$, $PH_4Br$, $PH_4I$, analogous to ammonium chloride, bromide, and iodide. The hydrides of arsenic and antimony exhibit no basic character. All the elements of this group unite with chlorine, giving rise to the compounds

$$NCl_3, PCl_3, AsCl_3, SbCl_3, BiCl_3,$$

which also exhibit a gradation in their properties: thus, nitrogen trichloride is an extremely unstable liquid, exploding with extraordinary violence upon very slight causes, while the analogous bismuth compound is a perfectly stable solid.

The boiling-points of these compounds show a gradual increase with the increasing atomic weight of the element: thus, nitrogen chloride boils at 71°, phosphorus trichloride at 78°, arsenic trichloride at 130.2°, and antimony trichloride at 200°.

The elements arsenic, antimony, and bismuth are isomorphous, and their corresponding compounds are also isomorphous.

The first member of this family, namely, nitrogen, has been already treated in Part II., as one of the four typical elements studied in that section of the book. It occupies a position in relation to the other members of the family, very similar to that of oxygen towards sulphur, selenium, and tellurium.

## PHOSPHORUS.

Symbol, P. Atomic weight = 30.96. Vapour density = 61.92.
Molecular weight = 123.94.

**History.**—Phosphorus was first discovered by the alchemist Brand, of Hamburg (1669), who obtained it by distilling a mixture ith urine which had been evaporated to a thick syrup. ss, however, was kept secret. Robert Boyle (1680) disıe process of obtaining this element, but the method was ;hed till after his death. Until the year 1771, when ublished a method by which phosphorus could be obm bone ash, this element was looked upon as a rare :uriosity. The name *phosphorus* was not first coined for :nt: it had been in previous use to denote various subıown at that time, which had the property of glowing in To distinguish the element it was called *Brand's phos-* · *English phosphorus.*

**ence.**—Phosphorus has never been found in nature :e state. In combination with oxygen and metals, as :s, it is very widely distributed, especially as calcium :. The following are some of the commonest natural :s—

| | |
|---|---|
| ›rerite, or estramadurite . | $Ca_3(PO_4)_2$. |
| ıte . . . . . . | $3Ca_3(PO_4)_2CaCl_2$. |
| :llite . . . . . | $2Al_2(PO_4)_2,Al_2(HO)_6,9H_2O$. |

ı phosphate is present in all fertile soils, being derived disintegration of rocks: the presence of phosphates in een shown to be essential to the growth of plants. From ıble it passes into the animal kingdom, where it is chiefly ı the urine, brain, and bones. Bones contain about 60 of calcium phosphate, to which they entirely owe their

**of Formation.**—*Manufacture.* The chief source of ıs is bone ash, a material obtained by burning bones, h consists of nearly pure calcium phosphate, $Ca_3(PO_4)_2$. rieties of calcium phosphate, such as sombrerite and re also employed, as well as phosphates of other metals, he Redonda phosphates, which consist of phosphates of alumina. The bone ash, in fine powder, is first decommeans of sulphuric acid, specific gravity 1.5 to 1.6. This is performed in large circular wooden vessels, resem:ewer's "mash tun," provided with an agitator, and into ;h pressure steam can be driven. Finely-ground bone ash ıuric acid, in charges of a few cwts. at a time, are alterrred into the decomposer, until from four to five tons of phosphate have been introduced, with sufficient acid to convert th *whole* of the lime into calcium sulphate, according to the equ tion—

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4.$$

The contents of the decomposer are next run out into filteri tanks, and the phosphoric acid is then concentrated to a syrup, i large lead-lined pans through which steam-coils pass, the liqu being constantly agitated by a mechanical stirrer.

The concentrated liquor is next mixed, either with sawdust, or with coarsely-ground charcoal, or coke, and the mixture completely dried by being heated in a cast-iron pot, or in a muffle, to a

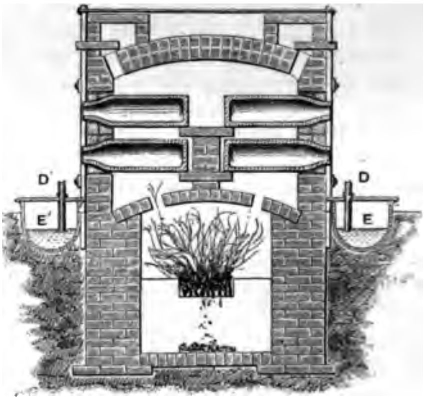

Fig. 114.

dull red heat. During this process, the tribasic phosphoric acid (or orthophosphoric acid), $H_3PO_4$, is converted by loss of water into metaphosphoric acid, $HPO_3$—

$$H_3PO_4 = H_2O + HPO_3.$$

The charred mixture is then distilled in bottle-shaped retorts of Stourbridge clay, about 3 feet long, and having an internal diameter of 8 inches. A number of these retorts, usually twenty-four, are arranged in two tiers, in a galley furnace, as seen in section in Fig. 114. The empty retorts are first gradually raised to a bright red heat, and a charge of the mixture is then quickly introduced. Bent pieces of 2-inch malleable iron pipe are then luted into the mouths of the retorts, connecting them with the pipes, D D′. These pipes dip into troughs of water, E E′, which run along the entire length of the furnace, and in which the phosphorus condenses. The temperature of the furnace is then raised to a white heat, when decomposition of the metaphosphoric acid commences, and phosphorus begins to distil over. The process is continued for about sixteen hours. The change that goes on is mainly represented by the following equation—

$$4HPO_3 + 12C = 12CO + 2H_2 + 4P.$$

The crude product, which is usually dark red or black in appearance, is first melted under hot water, and thoroughly stirred, in order to allow the greater part of the rougher suspended matters to rise to the surface. The mass is then allowed to resolidify. The exact processes by which phosphorus is further purified on a manufacturing scale are guarded as trade secrets : one method that has been in use, consists in treating the phosphorus while melted under water, with a mixture of potassium dichromate and sulphuric acid, whereby some of the impurities are oxidised, and others are caused to rise to the surface as a scum, leaving the phosphorus as a clear liquid beneath.

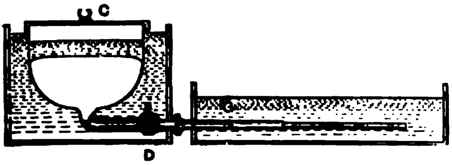

Fig. 115.

Phosphorus usually comes into commerce either in the form of wedges, or as sticks. The operation of casting the phosphorus into sticks is performed beneath water. A quantity of phosphorus beneath a shallow layer of water is placed in the vessel C, Fig. 115, which is contained in a tank of water through which a steam-coil passes. Connected to the phosphorus reservoir is a glass tube, G, which passes into a second shallow tank of cold water. On opening the cock D, the liquid phosphorus flows into the cold glass tube, where it congeals, and it may then be drawn through as a continuous rod of phosphorus, if care be taken not to draw it out faster than it solidifies. It is the custom to adopt a uniform length and thickness of stick, namely, 7½ inches long and ½ inch diameter. Nine such sticks weigh 1 lb.

**Properties.**—When freshly prepared and kept in the dark, phosphorus is a translucent, almost colourless, wax-like solid. Even in the dark it soon loses its transparency, and becomes coated with an opaque white film; while if exposed to the light, the film that forms becomes first yellow, then brown, and in time the phosphorus assumes a red and even a black colour throughout its entire mass. Its specific gravity at 16° is 1.82. At 0° phosphorus becomes moderately brittle, and a stick of it may be readily snapped, when its crystalline character will be seen. At 15° it becomes soft, and may be cut with a knife, like wax. Phosphorus melts under water at 43.3°, and the liquid exhibits the property of suspended solidification. If the melted material, which has been cooled below its solidifying point, be touched with a fragment of phosphorus upon the end of a capillary glass tube, the mass instantly congeals with rise of temperature.[*]

Phosphorus contained in a closed vessel, without water, melts at as low a temperature as 30°,[†] and when heated in air to 34° it takes fire. At a temperature of 269° phosphorus boils, and forms a colourless vapour.

Phosphorus is volatile at ordinary temperatures: if a small quantity of phosphorus be sealed in a vacuous tube, and the tube be placed in the dark, the phosphorus will slowly vaporise; and if one end of the tube be kept slightly cooler than the rest, the phosphorus will sublime upon that part, in the form of brilliant, colourless, and highly refracting rhombic crystals, which retain their beauty so long as they are kept in the dark. The density of the vapour of phosphorus is 61.92, giving a molecular weight of 123.94, which is four times the atomic weight, showing that the molecule of phosphorus contains four atoms. Even at temperatures as high as 1040 these tetratomic molecules are stable, but it has been shown that at higher temperatures, dissociation begins to take place.

On account of its ready inflammability, phosphorus is always preserved under water, which exerts practically no solvent action upon it. It is extremely soluble in carbon disulphide, 1 part of this quid dissolving 9.26 parts of phosphorus. On evaporation, the lement is deposited in the form of colourless crystals. Phosphorus s also soluble, but to a less extent, in chloroform, benzene, turpenine, alcohol, olive oil, and many other solvents. A solution of hosphorus in carbon disulphide, when allowed to evaporate upon piece of blotting-paper, leaves the element in so finely divided a ondition, that its rapid oxidation almost immediately raises the emperature to the ignition point of the phosphorus, when it akes fire.

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[*] See "Chemical Lecture Experiments," Nos. 510, 511.

[†] Readman.

On exposure to moist air in the dark, phosphorus appears faintly uminous, emitting a pale greenish-white light, and at the same ime evolving white fumes which possess an unpleasant, garlic-like mell, and are poisonous. These fumes consist mainly of phoshorous oxide, $P_4O_6$, and the glowing of the phosphorus is the esult of its oxidation ; phosphorus does not glow when placed n an inert gas which is perfectly free from admixed oxygen, lthough the presence of very small traces of free oxygen in such a as, is sufficient to cause the phosphorescence. At a few derees below 0°, phosphorus ceases to glow in the air. Although he glowing is due to oxidation, phosphorus does not appear uminous in pure oxygen at temperatures below about 15°. If, herefore, a stick of phosphorus which is glowing in the air, e immersed in a jar of oxygen, its phosphorescence is at once topped. If, however, the oxygen be slightly rarefied, the phoshorus again becomes luminous. Similarly, the phosphorescence hat is exhibited in air, is stopped if the air be compressed.* The low of phosphorus is believed to be associated with the formation f ozone, for the presence in the air of traces of such gases and apours as ethylene, turpentine, or ether, which are known to ossess the power of destroying ozone, at once stops the glowing f a stick of phosphorus.

Phosphorus is incapable of uniting with oxygen if the gas be erfectly pure and free from aqueous vapour. It has been shown hat in oxygen which has been dried by prolonged exposure to the esiccating action of phosphorus pentoxide, phosphorus may not nly be melted, but even distilled, without any combination with he oxygen taking place.

If water, beneath which is a small quantity of melted phosphorus, e boiled, the phosphorus vaporises with the steam, and renders the steam luminous: use is made of this property, as a means of detecting free phosphorus, in toxicological analysis.

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* "Chemical Lecture Experiments," Nos. 413 to 417.

Phosphorus is a powerfully poisonous substance; in large doses it causes death in a few hours, in smaller quantities it produces stomachic pains and sickness, usually ending in convulsion. Persons constantly exposed to the vapours arising from the handling of phosphorus, either in its manufacture or in the manufacture of matches, are very liable to suffer from caries of the bones of the jaw and nose; it is believed that this injurious effect is caused by the white fumes which are the product of oxidation, and not by the actual vapour of phosphorus.

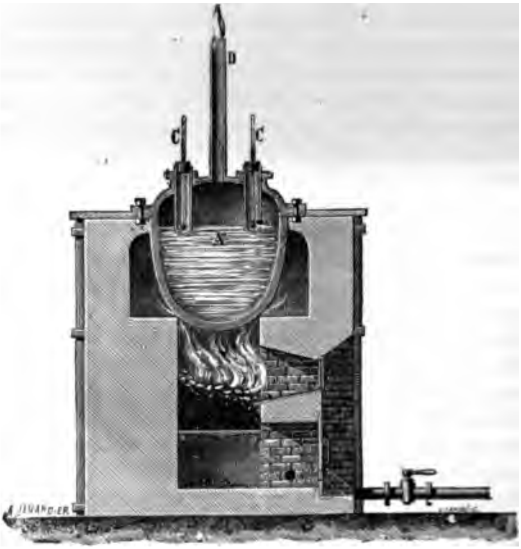


FIG. 116.

**Red Phosphorus.**—When phosphorus is heated to a temperature between 240° and 250°, out of contact with air, it passes into an allotropic modification. The same transformation takes place when phosphorus is heated to 200° with an extremely small proportion of iodine.

Red phosphorus is manufactured by heating ordinary phosphorus in a cast-iron pot, provided with a cover, through which passes a short open pipe, D (Fig. 116). The pot is carefully and uniformly heated to between 240° and 250°, as indicated by the thermometers C C′, which are encased in metal tubes, to prevent the phosphorus from attacking the glass. A small quantity of the phosphorus becomes oxidised by the air within the vessel, but after this atmospheric oxygen is used up, no further oxidation takes place. If the temperature be allowed to rise above 260°, the red phosphorus is reconverted into the ordinary modification, and with the evolution of so much heat, that unless the open tube be provided, as a safety-valve, the iron vessel is liable to burst. The material that is obtained at the end of the operation, is in the form of hard, solid lumps, which still contain a certain amount of the unchanged phosphorus mixed with them. It is first ground to powder beneath water, and then boiled with a solution of sodium hydroxide (caustic soda), to remove the ordinary phosphorus, and finally washed and dried.

**Properties.**—Red phosphorus, as usually sent into commerce, is a chocolate-red powder, having a specific gravity of 2.25. It is not luminous in the dark, and has no taste or smell. It is not poisonous, and when taken into the system is excreted unchanged. It is not soluble in carbon disulphide, or in any of the solvents which dissolve ordinary phosphorus. Red phosphorus is unaffected by exposure to dry air or oxygen, but in the presence of moisture it is very slowly oxidised. If red phosphorus which has been perfectly freed from ordinary phosphorus, and carefully washed and dried, be exposed to air and moisture, it is found after the lapse of some time to have become acid, owing to slight oxidation into phosphoric acid. When heated in contact with air, red phosphorus does not ignite below a temperature of 240°. Red phosphorus may be obtained in the form of rhombohedral crystals by heating the substance under pressure to a temperature of 580°.

The chief use of phosphorus is in the manufacture of matches. When ordinary phosphorus is employed, the bundles of wooden splints are first tipped with melted paraffin wax, and afterwards dipped into a paste, made of an emulsion of phosphorus, chlorate of potash, and glue. Matches so made, ignite when rubbed upon any rough surface; the paraffin (which is sometimes replaced by sulphur) serving to transmit the combustion from the phosphorus to the wood. Since the discovery of red phosphorus, and its non-injurious properties, the old phosphorus match has been largely superseded by the so-called *safety matches*. In these matches the splints are tipped with a mixture of potassium chlorate, potassium dichromate, red lead, and antimony sulphide, and they are ignited by being rubbed upon a prepared surface, consisting of a mixture of antimony sulphide and red phosphorus. Although these matches will not ignite by ordinary friction upon any but the specially prepared surface, they may be inflamed by being swiftly drawn along a sheet of ground glass, or strip of linoleum.

## *COMPOUNDS OF PHOSPHORUS WITH HYDROGEN.*

Three compounds of phosphorus and hydrogen are known, namely—

$PH_3$ (gaseous); $P_2H_4$ (liquid); and $P_4H_2$(?) (solid).

### GASEOUS PHOSPHORETTED HYDROGEN (*Hydrogen phosphide: Phosphine*).

Formula, $PH_3$. Molecular weight = 33.96. Density = 16.98.

**Modes of Formation.**—(1.) This substance is formed when red phosphorus is gently heated in a stream of hydrogen.

(2.) It may be prepared by boiling phosphorus with a solution of potassium or sodium hydroxide—

$$3NaHO + 4P + 3H_2O = 3NaH_2PO_2 + PH_3.$$

In this reaction a small quantity of the liquid hydride ($P_2H_4$) is simultaneously formed, which imparts to the gas the property of spontaneous inflammability. It also contains a certain quantity of free hydrogen, produced by the action of the caustic alkali upon the sodium hypophosphite, thus—

$$NaH_2PO_2 + 2NaHO = 2H_2 + Na_3PO_4.$$

To obtain the gas by this method, a quantity of a strong solution of caustic soda, and a few fragments of phosphorus, are placed in a flask, fitted as shown in Fig. 117. A stream of coal gas is passed through the apparatus, in order to displace the air, and the solution is gently heated. Phosphoretted hydrogen is readily disengaged, and as each bubble escapes into the air, it bursts into flame, and forms a vortex ring of white smoke of phosphoric acid.

If alcoholic potash be substituted for the aqueous solution in this reaction, the liquid phosphoretted hydrogen is dissolved in the alcohol, and the gas which is evolved is therefore not spontaneously inflammable.*

(3.) Phosphoretted hydrogen is also produced by the action of water upon calcium phosphide—

$$3P_2Ca_2 + 12H_2O = 6Ca(HO)_2 + 4PH_3 + 2P.$$

A secondary reaction, by which liquid phosphoretted hydrogen is formed, goes on simultaneously—

$$P_2Ca_2 + 4H_2O = 2Ca(HO)_2 + P_2H_4.$$

The gas, therefore, that is evolved is spontaneously inflammable.

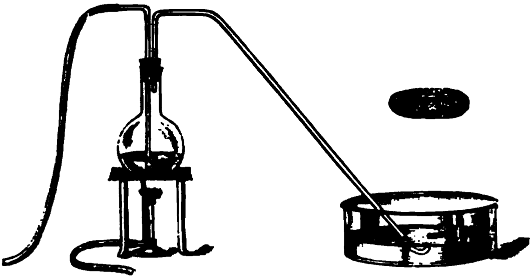


FIG. 117.

(4.) Pure gaseous phosphoretted hydrogen may be prepared by the action of potassium hydroxide upon phosphonium iodide—

$$PH_4I + KHO = KI + H_2O + PH_3.$$

**Properties.**—Gaseous phosphoretted hydrogen, or phosphine, is a colourless gas, having an offensive smell resembling rotting fish. It is not spontaneously inflammable, but its ignition temperature is below 100° C. (see page 291). The gas burns with a brightly luminous flame, producing water and metaphosphoric acid—

$$PH_3 + 2O_2 = HPO_3 + H_2O.$$

When burnt in oxygen the flame is extremely dazzling.

The gas is not acted upon by oxygen at ordinary temperatures and pressures, but if a mixture of these gases be suddenly rarefied, combination at once takes place with explosion. Phosphoretted hydrogen is decomposed by chlorine or bromine, a jet of the gas spontaneously igniting when introduced into chlorine, or the vapour of bromine—

---

* See "Chemical Lecture Experiments," No. 527.

$$PH_3 + 4Cl_2 = 3HCl + PCl_5.$$

The gas is also decomposed by iodine, but in this case the action is less energetic, and a portion of the hydriodic acid which is produced, unites with the phosphine and forms phosphonium iodide, thus—

$$(1.)\ PH_3 + 3I_2 = PI_3 + 3HI.$$
$$(2.)\ PH_3 + HI = PH_4I.$$

Phosphine is a highly poisonous gas, and the inhalation of even small quantities of it is attended with injurious effects. It is slightly soluble in water, and imparts its own smell and an unpleasant taste to the liquid. The solution decomposes after a short time, especially in the light, and deposits red phosphorus.

Phosphoretted hydrogen has no action upon either litmus or turmeric paper, but it resembles its nitrogen analogue, ammonia, in combining with hydrochloric, hydrobromic, and hydriodic acids, forming respectively phosphonium chloride, bromide, and iodide.

**Phosphonium Chloride,** $PH_4Cl$.—When a mixture of phosphine and gaseous hydrochloric acid is passed through a tube immersed in a freezing mixture, the gases unite and form a white crystalline incrustation upon the tube. If the tube be afterwards sealed up, the compound may be sublimed from one part of the tube to another, when it crystallises in large, brilliant, transparent cubes. If the tube be opened, the compound rapidly dissociates into its two generators. This compound may also be obtained by subjecting a mixture of the two gases to pressure. Under a pressure of about eighteen atmospheres at the ordinary temperature, crystals of phosphonium chloride are deposited; and as the pressure is released the crystals gradually dissociate again.

**Phosphonium Bromide,** $PH_4Br$. — Phosphoretted hydrogen combines with hydrobromic acid at ordinary temperatures and pressures, but as the compound begins to dissociate at the ordinary temperature, the combination is only completely brought about by cooling the gases. Phosphonium bromide may be readily prepared by passing the two gases into a flask immersed in a moderate freezing mixture. The salt may be obtained in the form of large transparent cubical crystals by sublimation in a sealed vessel.

**Phosphonium Iodide,** $PH_4I$.—This compound may be obtained by a method similar to that given for the preparation of the bromide. It is also produced when phosphoretted hydrogen is passed over iodine, as already mentioned. It is most readily prepared by the action of water upon a mixture of phosphorus and iodine. For this purpose ten parts of phosphorus are dissolved in carbon disulphide in a tubulated retort, to which seventeen parts of iodine are gradually added, the retort being kept cold. The carbon disulphide is then distilled off from a water-bath, a stream of carbon dioxide being passed through the apparatus towards the end of the distillation, to assist in expelling the last traces of the disulphide.

Six parts of water are then gradually introduced from a dropping funnel, when a brisk action takes place, and the phosphonium iodide produced is volatilised, and may be condensed in a long wide glass tube connected to the retort. Hydriodic acid is at the same time formed—

$$9I + 13P + 24H_2O = 7PH_4I + 2HI + 6H_3PO_4.$$

The phosphonium iodide condenses in the form of brilliant quadratic prisms.

**Liquid Phosphoretted Hydrogen,** $P_2H_4$.—This compound is obtained in small quantities, when phosphorus is boiled with a solution of caustic soda. It is obtained in large quantities, by the decomposition of calcium phosphide with water, by the reaction already mentioned. In order to collect the compound, a quantity of calcium phosphide is introduced into a flask provided with a dropping funnel and exit tube. After displacing the air from the apparatus by an inert gas, water is gradually introduced from the funnel, and the products of the reaction, after passing through a small empty tube, where water is arrested, are passed through a U-tube immersed in a freezing mixture, where the liquid phosphoretted hydrogen condenses.

**Properties.**—Liquid phosphoretted hydrogen is a colourless, highly refracting, and spontaneously inflammable liquid. On exposure to light it is quickly decomposed into the gaseous and the solid hydrides of phosphorus—

$$5P_2H_4 = P_4H_2 + 6PH_3.$$

The formation of a spontaneously inflammable gas by the action of water upon calcium phosphide, has found a practical application in the marine appliance known as "Holmes' signal." This consists of a tin canister filled with lumps of calcium phosphide. A metal tube, closed at the bottom with a piece of block tin, enters the canister from below, and a short cone of the same soft metal is soldered upon the top. When the signal is to be used, it is securely fixed into a wooden float, Fig. 118. The cone is cut off, and a hole punctured through the bottom of the tube below, and the apparatus thrown into the sea. The phosphoretted hydrogen spontaneously ignites and burns with a large brilliant flame from the top of the tin, illuminating a considerable area.

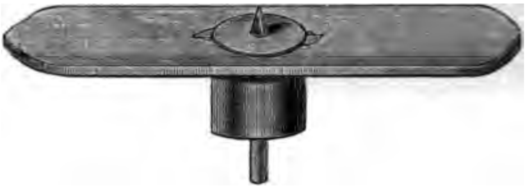


FIG. 118.

**Solid Phosphoretted Hydrogen,** $P_4H_2$(?)—The composition of this compound is not known with certainty. It is a yellow powder, obtained, as already mentioned, by the spontaneous decomposition of the liquid compound.

## COMPOUNDS OF PHOSPHORUS WITH THE HALOGENS.

Phosphorus combines with all the halogen elements, forming the following compounds—

| | | | |
|---|---|---|---|
| $PF_3$ | $PCl_3$ | $PBr_3$ | $PI_3$. |
| $PF_5$ | $PCl_5$ | $PBr_5$ | $P_2I_4$. |

**Phosphorus Trifluoride,** $PF_3$, is obtained by the action of arsenic trifluoride upon phosphorus trichloride—

$$AsF_3 + PCl_3 = PF_3 + AsCl_3.$$

It is more conveniently prepared by gently heating a mixture of zinc fluoride and phosphorus tribromide—

$$3ZnF_2 + 2PBr_3 = 2PF_3 + 3ZnBr_2.$$

**Properties.**—Phosphorus trifluoride is a colourless, pungent-smelling gas. It has no action upon glass in the cold, but when heated it forms silicon fluoride and phosphorus. It is moderately soluble in water. Phosphorus trifluoride unites directly with bromine, forming the compound $PF_3Br_2$.

**Phosphorus Pentafluoride,** $PF_5$.—This compound is formed when phosphorus burns in fluorine. It is best prepared by the action of arsenic trifluoride upon phosphorus pentachloride—

$$5AsF_3 + 3PCl_5 = 3PF_5 + 5AsCl_3.$$

**Properties.**—Phosphorus pentafluoride is a heavy, colourless gas, which fumes strongly in moist air, being decomposed by water into hydrofluoric and phosphoric acids—

$$PF_5 + 4H_2O = 5HF + H_3PO_4.$$

Owing to this decomposition it has a pungent and irritating effect upon the mucous membrane.

It is not acted upon by oxygen, but unites directly with dry gaseous ammonia, forming a white solid compound having the composition $2PF_5,5NH_3$.

Phosphorus pentafluoride is an extremely stable compound, being capable of withstanding a very high temperature without dissociation. On this account it is of special interest, as affording an example of a compound in which phosphorus is united to five monovalent atoms to form a stable substance. The corresponding chlorine and bromine compounds readily dissociate, when heated, into compounds containing trivalent phosphorus and the free halogen.

**Phosphorus Trichloride,** $PCl_3$.—This compound is prepared by passing dry chlorine over red phosphorus, gently heated in a tubulated retort. The two elements readily combine, and the volatile trichloride, mixed with more or less of the pentachloride, distils off, and is collected in a well-cooled receiver. The product is freed from the higher chloride by redistillation over ordinary phosphorus.

**Properties.** — Phosphorus trichloride is a colourless, mobile liquid, which boils at 75.95°. It has a pungent smell, and fumes strongly in moist air. Water at once decomposes it into hydrochloric and phosphorous acids—

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

**Phosphorus Pentachloride,** $PCl_5$.—This compound is formed when phosphorus burns in excess of chlorine. It is prepared by the action of chlorine upon the trichloride. Dry chlorine is passed on to the surface of a quantity of the trichloride, contained in a flask which is kept cool. The absorption of the chlorine is attended with considerable rise of temperature, and the contents of the flask rapidly become converted into a dry, pale yellow solid.

Phosphorus pentachloride is conveniently obtained by passing chlorine through a solution of phosphorus in carbon disulphide, the solution being kept cold.

**Properties.**—Phosphorus pentachloride is a yellowish-white, crystalline solid, having a pungent and irritating odour. It fumes strongly in contact with moist air, being decomposed by moisture into hydrochloric acid and phosphorus oxychloride—

$$PCl_5 + H_2O = 2HCl + POCl_3.$$

With excess of water, both phosphorus oxychloride and phosphorus pentachloride dissolve with evolution of heat, forming hydrochloric and phosphoric acids—

$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl.$$
$$PCl_5 + 4H_2O = H_3PO_4 + 5HCl.$$

Phosphorus pentachloride readily sublimes, without melting, at a temperature below that of boiling water. It can only be melted by being heated under pressure, to a temperature of 148°.

As the vapour of phosphorus pentachloride is heated, the compound dissociates into phosphorus trichloride and free chlorine. At 300° this dissociation is complete, and the vapour consists of equal molecules of the trichloride and chlorine. The gradual breaking down of the molecules of pentachloride, is seen from the following table, which gives the densities of the gas at different temperatures—

| Temperatures | 182° | 200° | 250° | 300° |
|---|---|---|---|---|
| Density . . | 72.5 | 69.2 | 57.0 | 51.95 |

At 300° it consists of molecules of $PCl_3$ (molecular weight = 137.07), and molecules of chlorine (molecular weight = 70.74), in equal numbers, which theoretically gives the molecular weight—

$$\frac{137.07 + 70.74}{4} = 51.95.$$

Phosphorus pentachloride is an important chemical reagent, inasmuch as by its action upon oxyacids, both inorganic and organic, the (HO) group in the acid can be replaced by chlorine. Thus with sulphuric acid, chlorosulphuric acid is formed—

$$\left.\begin{matrix}HO\\HO\end{matrix}\right\}SO_2 + PCl_5 = \left.\begin{matrix}Cl\\HO\end{matrix}\right\}SO_2 + POCl_3 + HCl.$$

With acetic acid it yields acetyl chloride—

$$\left.\begin{matrix}HO\\CH_3\end{matrix}\right\}CO + PCl_5 = \left.\begin{matrix}Cl\\CH_3\end{matrix}\right\}CO + POCl_3 + HCl.$$

It also effects the replacement of (HO) by chlorine, in alcohols. Thus, with ethyl alcohol (spirits of wine) it forms ethyl chloride—

$$\left.\begin{matrix}HO\\CH_3\end{matrix}\right\}CH_2 + PCl_5 = \left.\begin{matrix}Cl\\CH_3\end{matrix}\right\}CH_2 + POCl_3 + HCl.$$

**Phosphorus Tribromide,** $PBr_3$, is best prepared by dropping bromine upon an excess of red phosphorus. It forms a colourless pungent-smelling liquid, which boils at 172.9°.

**Phosphorus Pentabromide,** $PBr_5$, is prepared by adding bromine to the tribromide. It is a yellow solid, which melts to a reddish liquid. It is very unstable, being dissociated below 100° into its generators, the tribromide and bromine.

**Diphosphorus Tetriodide** (*phosphorus di-iodide*), $P_2I_4$.—This substance is prepared by the gradual addition of 8.2 parts of iodine to 1 part of phosphorus dissolved in carbon disulphide. On gently distilling off the carbon disulphide, the iodide is left as a yellow crystalline solid. The compound melts at 110°.

**Phosphorus Tri-iodide,** $PI_3$, is obtained by employing a larger proportion of iodine in the above reaction. It is a solid substance, crystallising in red six-sided prisms, which are decomposed by water into hydriodic and phosphorous acids.

## *OXY AND THIO COMPOUNDS OF PHOSPHORUS AND THE HALOGENS.*

The following compounds are known, containing phosphorus combined with the halogens, and either oxygen or sulphur—

$POF_3$; $POCl_3$; $P_2O_3Cl_4$; $POBrCl_2$; $POBr_3$.
$PSF_3$; $PSCl_3$; — — $PSBr_3$.

These compounds may be regarded as derived from the haloid compounds, *by the replacement* of two atoms of the halogen by an equivalent of oxygen, or of divalent sulphur; or they may be viewed as derivatives of phosphoric acid, by the substitution of halogen elements in the place of (HO) groups. The tribasic phosphoric acid, $PO(HO)_3$, may be regarded as giving rise to the compounds $POF_3$, $POCl_3$, &c.; while the compound, $P_2O_3Cl_4$, may be viewed as a derivative of pyrophosphoric acid, $P_2O_3(HO)_4$.

**Phosphoryl Fluoride** (*phosphorus oxyfluoride*), $POF_3$, may be obtained by the action of phosphoryl chloride ($POCl_3$) upon zinc fluoride—

$$3ZnF_2 + 2POCl_3 = 2POF_3 + 3ZnCl_2.$$

It may also be prepared by gently heating a mixture of finely powdered cryolite and phosphorus pentoxide—

$$2(AlF_3,3NaF) + 2P_2O_5 = 4POF_3 + Al_2O_3 + 3Na_2O.$$

Phosphoryl fluoride is a colourless gas, which fumes in the air, and is decomposed by water. The gas in a dry condition does not attack glass.

**Thiophosphoryl Fluoride**, $PSF_3$, is most readily prepared by gently heating in a leaden tube, a mixture of dry lead fluoride and phosphorus pentasulphide—

$$3PbF_2 + P_2S_5 = 3PbS + 2PSF_3.$$

The gas may be collected over mercury.

Thiophosphoryl fluoride is a colourless gas, which spontaneously inflames when a jet of it is allowed to escape into the air. It burns with a pale greenish non-luminous flame. In pure oxygen the gas burns with a yellow and more luminous flame. The gas is decomposed by heat, into phosphorus fluoride, phosphorus, and sulphur. When heated in a glass vessel, sulphur and phosphorus are deposited, and silicon tetrafluoride is formed—

$$4PSF_3 + 3Si = 3SiF_4 + 4P + 4S.$$

**Phosphoryl Chloride** (*phosphorus oxychloride*), $POCl_3$.—This compound is formed, by the first action of water upon phosphorus pentachloride (*q.v.*). It is also obtained when phosphorus pentachloride and pentoxide are heated together in a sealed tube—

$$3PCl_5 + P_2O_5 = 5POCl_3.$$

It is most readily prepared by heating phosphorus pentachloride with either oxalic acid, or boric acid, thus—

$$PCl_5 + H_2C_2O_4 = POCl_3 + 2HCl + CO_2 + CO.$$
$$3PCl_5 + 2H_3BO_3 = 3POCl_3 + 6HCl + B_2O_3.$$

**Properties.**—Phosphoryl chloride is a colourless fuming liquid, which boils at 107.23°. When cooled to about −10° it solidifies to a white crystalline mass, which melts at 0.8°. It is decomposed by water with formation of tribasic phosphoric acid and hydrochloric acid—

$$POCl_3 + 3H_2O = PO(HO)_3 + 3HCl.$$

**Pyrophosphoryl Chloride,** $P_2O_3Cl_4$, is obtained by passing nitrogen peroxide through phosphorus trichloride, and subsequently distilling the liquid. The reaction is complicated, and cannot be expressed by a single equation; nitrogen is evolved, and phosphorus pentoxide, nitrosyl chloride, and phosphoryl chloride are simultaneously formed. Pyrophosphoryl chloride is a colourless fuming liquid, boiling between 210° and 215°. It is decomposed by water, and forms hydrochloric acid and orthophosphoric acid (*not pyrophosphoric acid*)—

$$P_2O_3Cl_4 + 5H_2O = 2H_3PO_3 + 4HCl.$$

It is converted by phosphorus pentachloride into phosphoryl chloride—

$$P_2O_3Cl_4 + PCl_5 = 3POCl_3.$$

**Thiophosphoryl Chloride,** $PSCl_3$, is prepared by heating a mixture of phosphorus pentasulphide and pentachloride—

$$3PCl_5 + P_2S_5 = 5PSCl_3.$$

It is a colourless liquid, boiling at 125°. It fumes in moist air, being decomposed by water into sulphuretted hydrogen, phosphoric and hydrochloric acids—

$$PSCl_3 + 4H_2O = H_2S + H_3PO_4 + 3HCl.$$

## OXIDES AND OXYACIDS OF PHOSPHORUS.

Four compounds of phosphorus and oxygen are known, all of which are formed when phosphorus is burned in a limited supply of air—

| | |
|---|---|
| Phosphorus monoxide | $P_4O$. |
| Phosphorous oxide (phosphorus trioxide) | $P_4O_6$. |
| Phosphorus tetroxide | $P_2O_4$. |
| Phosphorus pentoxide | $P_2O_5$. |

The two compounds, phosphorus trioxide and pentoxide, are the best known of these oxides, and they give rise respectively to phosphorous and phosphoric acids. The following oxyacids of phosphorus are known—

| | | | Corresponding Oxide. |
|---|---|---|---|
| Hypophosphorous acid | $H_3PO_2$ | — | — |
| Phosphorous acid | $H_3PO_3$ | or $P(HO)_3$ | $P_4O_6$ |
| Orthophosphoric acid | $H_3PO_4$ | „ $PO(HO)_3$ | $P_2O_5$ |
| Pyrophosphoric acid | $H_4P_2O_7$ | „ $P_2O_3(HO)_4$ | |
| Metaphosphoric acid | $HPO_3$ | „ $PO_2(HO)$ | |

**Phosphorus Monoxide,** $P_4O$.—When phosphorus is burned in a tube through which a slow stream of air is caused to pass, a portion of the phosphorus is converted into the monoxide, which forms an orange red solid substance.

**Phosphorous Oxide** (*phosphorous anhydride*), $P_4O_6$; molecular weight = 221.52.—This oxide is obtained, mixed with a large excess of the pentoxide, when phosphorus is burned in a tube through which a regulated stream of air is passed. In order to obtain the compound in a state of purity, the following method is employed. A quantity of phosphorus is introduced into a glass tube, bent in the manner indicated in Fig. 119, and fitted into one end of a long, wide, Liebig's condenser. Into the end of the condenser nearest to the U-tube, there is introduced a loose plug of glass wool, which serves to arrest the pentoxide. The phosphorus is ignited at the open end of the glass tube, and a stream of air drawn through the apparatus by means of an aspirator. A stream of water, at 60°, is circulated through the condenser, when the easily fusible phosphorous oxide is carried over, and condenses in the U-tube, which is immersed in a freezing mixture.

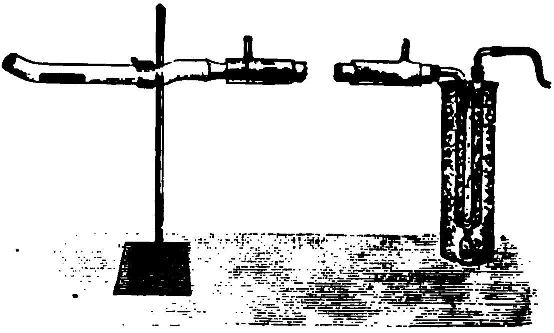


Fig. 119.

**Properties.**—Phosphorous oxide, as it collects in the cooled tube, is a snow-white crystalline solid, which melts at 22.5° to a colourless liquid. The liquid solidifies at 21° to a white, waxy-looking mass, consisting of monoclinic prismatic crystals. The liquid boils at 173.1°. It possesses an unpleasant garlic smell, and is highly poisonous. Phosphorous oxide is only very slowly acted upon by cold water, which gradually dissolves it, forming phosphorous acid—

$$P_4O_6 + 6H_2O = 4H_3PO_3.$$

In contact with hot water a violent action takes place, in which spontaneously inflammable phosphoretted hydrogen is evolved, and a red deposit, consisting of red phosphorus and phosphorus monoxide, is formed.

When heated in a sealed tube to a temperature of 440°, phosphorous oxide is decomposed into phosphorus tetroxide, and red phosphorus—

$$2P_4O_6 = 3P_2O_4 + 2P.$$

When exposed to air or oxygen, phosphorous oxide is gradually oxidised into phosphorus pentoxide, but when placed in warm oxygen it bursts into flame. When brought into chlorine it also spontaneously inflames.

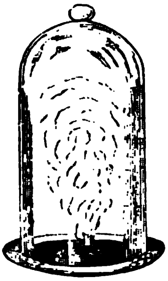


FIG. 120.

**Phosphorus Tetroxide**, $P_2O_4$.—This substance is obtained when phosphorous oxide is heated in a sealed tube to a temperature of 440°. It forms brilliant transparent crystals, which appear as a sublimate in the tube. This oxide is highly deliquescent, and dissolves in water with evolution of heat.

**Phosphorus Pentoxide**, $P_2O_5$; molecular weight = 141.82.—This oxide is the main product of the combustion of phosphorus in air or oxygen. It may readily be obtained, by burning a quantity of phosphorus in a small capsule, and covering the whole with a large bell-jar, Fig. 120. The white clouds of phosphorus pentoxide collect as a soft snow-like substance.

**Properties.**—Phosphorus pentoxide is a white, amorphous, and very voluminous powder. It is without smell, although as usually prepared it frequently possesses a slight garlic odour, owing to the presence of phosphorous oxide.

Phosphorus pentoxide is extremely hygroscopic, absorbing moisture from the air with great rapidity. It must therefore be preserved either in well-fitting stopper bottles, or in hermetically sealed vessels. Its affinity for water, constitutes it the most useful desiccating agent known to chemists: prolonged exposure to phosphoric pentoxide, removes the last traces of aqueous vapour from gases.

When thrown into water, phosphorus pentoxide is dissolved with a hissing sound, resembling the quenching of hot iron, and forms metaphosphoric acid—

$$P_2O_5 + H_2O = 2HPO_3,$$

which gradually passes into orthophosphoric acid—

$$HPO_3 + H_2O = H_3PO_4.$$

Phosphorus pentoxide is capable of abstracting the elements of water from a number of substances, both inorganic and organic; thus, it converts nitric acid into nitrogen pentoxide—

$$2HNO_3 - H_2O = N_2O_5.$$

In the same way it withdraws the elements of water from alcohol, with the evolution of ethylene—

$$C_2H_6O - H_2O = C_2H_4.$$

**Hypophosphorous Acid,** $H_3PO_2$.—This acid is prepared by the action of sulphuric acid upon the barium salt—

$$Ba(H_2PO_2)_2 + H_2SO_4 = BaSO_4 + 2H_3PO_2.$$

The solution, after the removal of the barium sulphate by filtration, is gently heated until its temperature rises to 130°, when it will be sufficiently concentrated to deposit crystals, when cooled to 0°.

The barium hypophosphite is obtained by boiling phosphorus with a solution of barium hydroxide—

$$3Ba(HO)_2 + 8P + 6H_2O = 2PH_3 + 3Ba(H_2PO_2)_2.$$

**Properties.**—Hypophosphorous acid is a white crystalline compound, which melts at 17.4°. When strongly heated, it is converted into orthophosphoric acid with the evolution of gaseous phosphoretted hydrogen—

$$2H_3PO_2 = H_3PO_4 + PH_3.$$

Hypophosphorous acid acts as a powerful reducing agent, on account of the readiness with which it absorbs oxygen and is converted into orthophosphoric acid—

$$\left.\begin{matrix}H\\H\\HO\end{matrix}\right\}PO + O_2 = \left.\begin{matrix}HO\\HO\\HO\end{matrix}\right\}PO \text{ ; or } \left.\begin{matrix}H\\HO\\HO\end{matrix}\right\}P + O_2 = \left.\begin{matrix}HO\\HO\\HO\end{matrix}\right\}PO.$$

Hypophosphorous acid is a feeble monobasic acid ; its salts with monovalent metals being represented by the formula $MH_2PO_2$.

It is customary to express the basicity of oxyacids by the number of (HO) groups that are contained in the molecule, and as this acid is monobasic its constitution would be expressed by the formula $POH_2(HO)$. Many of the oxyacids of phosphorus, however, show a tendency to exhibit a lower degree of basicity than is represented by the number of (HO) groups they contain; thus, orthophosphoric acid, $PO(HO)_3$, which is tribasic, and forms the salt trisodium phosphate, $PO(NaO)_3$, holds the third atom of the metal so loosely, that even such a feeble acid as carbonic acid is capable of expelling it—

$$PO(NaO)_3 + CO_2 + H_2O = PO(HO)(NaO)_2 + HNaCO_3.$$

or—

$$Na_3PO_4 + CO_2 + H_2O = HNa_2PO_4 + HNaCO_3.$$

The weaker acid, phosphorous acid, is also tribasic, $P(HO)_3$, and forms trisodium phosphite, $P(NaO)_3$, or $Na_3PO_3$. But this salt is even decomposed by water, into the disodium phosphite, $P(HO)(NaO)_2$, or $HNa_2PO_3$.

Hypophosphorous acid being a still weaker acid, its acidic power is destroyed as soon as one atom of hydrogen is replaced by a base, and its constitution may, in harmony with these facts, be expressed by the formula $PH(HO)_2$, or $\left.\begin{matrix}H\\HO\\HO\end{matrix}\right\}P$.

**Phosphorous Acid,** $H_3PO_3$, or $P(HO)_3$.—As already mentioned, this acid is formed when phosphorous oxide is dissolved in cold water.

It is most readily prepared by the action of water upon phosphorus trichloride—

$$PCl_3 + 3H_2O = 3HCl + P(HO)_3.$$

The production and decomposition of the phosphorus trichloride may be carried on simultaneously, by passing a stream of chlorine through phosphorus which is melted beneath water. The solution is evaporated until its temperature rises to 180°, when the liquid will have become so concentrated that on cooling it solidifies to a crystalline solid.

**Properties.**—Phosphorous acid is a white crystalline substance which melts at 70.1°. When heated, it decomposes into orthophosphoric acid, with evolution of phosphoretted hydrogen—

$$4H_3PO_3 = 3H_3PO_4 + PH_3.$$

Like hypophosphorous acid this compound absorbs oxygen, and therefore is a powerful reducing agent; silver salts are reduced to metallic silver, and mercuric salts are reduced to mercurous salts. By the absorption of oxygen it is converted into orthophosphoric acid—

$$H_3PO_3 + O = H_3PO_4.$$

Although a tribasic acid, its tribasic salts are unstable; the sodium compound, $Na_3PO_3$, which is the most stable inorganic salt, is decomposed by water into the dibasic salt—

$$Na_3PO_3 + H_2O = HNa_2PO_3 + NaHO.$$

$$\text{or} \qquad \left.\begin{matrix}NaO\\NaO\\NaO\end{matrix}\right\}P + H_2O = \left.\begin{matrix}HO\\NaO\\NaO\end{matrix}\right\}P + NaHO.$$

**Orthophosphoric Acid,** $H_3PO_4$, or $PO(HO)_3$.—This acid is formed when phosphorus pentoxide is dissolved in boiling water, or when the solution of the oxide in cold water is boiled—

$$P_2O_5 + 3H_2O = 2H_3PO_4.$$

Orthophosphoric acid is readily obtained by the oxidation of red phosphorus with nitric acid. Copious red fumes are evolved, and phosphoric acid remains in solution.

Phosphoric acid is prepared on a large scale by the action of sulphuric acid upon bone ash, as in the process for the manufacture of phosphorus—

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4.$$

The calcium sulphate is removed by filtration, and the solution orated to a syrup. Prepared in this way the acid usually ains arsenic. This is removed by first reducing it to arsenious e, by means of sulphur dioxide, and after boiling off the excess ılphur dioxide, precipitating the arsenic as sulphide by means lphuretted hydrogen.

**operties.**—The solution obtained by these methods is either entrated in vacuo, or heated to a temperature of 140°, and ved to cool, when the acid is obtained in the form of transnt six-sided prismatic crystals, belonging to the rhombic m. The substance is deliquescent, and melts at 38.6°.

ıosphoric acid is tribasic, and forms three series of salts, rding as one, two, or three of its hydrogen atoms are replaced n equivalent of metal. Thus, with the metal sodium the three are known—

| | |
|---|---|
| risodium phosphate (normal sodium phosphate) | $Na_3PO_4$. |
| Iydrogen disodium phosphate . . . . | $HNa_2PO_4$. |
| )ihydrogen sodium phosphate . . . . | $H_2NaPO_4$. |

ıe hydrogen may be replaced by its equivalent of more than base. Thus, the well-known compound, *microcosmic salt*, is ogen sodium ammonium phosphate, $HNa(NH_4)PO_4$. The which is precipitated when magnesium sulphate (in the pree of ammonium chloride and ammonia) is added to a solution phosphate, consists of the compound ammonium magnesium ıphate $(NH_4)MgPO_4$.

ıe heavy metals usually only form normal phosphates. Thus, he addition of silver nitrate to a solution of either of the three um salts, the same silver salt is precipitated, namely, trintic phosphate.

$$Na_3PO_4 + 3AgNO_3 = Ag_3PO_4 + 3NaNO_3.$$

[*] $$HNa_2PO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3.$$

$$H_2NaPO_4 + 3AgNO_3 = Ag_3PO_4 + NaNO_3 + 2HNO_3.$$

**rophosphoric Acid,** $H_4P_2O_7$, or $P_2O_3(HO)_4$.—This acid is

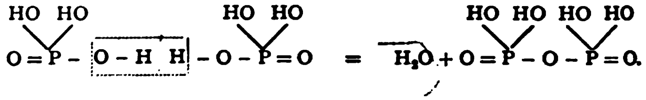
---

Iydrogen disodium phosphate, although belonging to that class of comds commonly called *acid salts*, on account of the fact that it still retains tion of the replaceable hydrogen of the acid, is strongly *alkaline* in its n upon litmus: silver nitrate is a neutral compound, hence in this reaction, ıixing an alkaline and a neutral liquid, an *acid* liquid is obtained, on ınt of the molecule of nitric acid that is set free.

derived from orthophosphoric acid, by the withdrawal of one molecule of water from two molecules of the acid. This change is effected by heating the *ortho* acid to 213°—

$$2H_3PO_4 - H_2O = H_4P_2O_7.$$

The formation of this acid from two molecules of orthophosphoric acid will be made clear by the following formulæ—



$$\mathrm{O=\overset{HO\ HO}{P}-\boxed{O-H\ \ H}-O-\overset{HO\ HO}{P}=O \;=\; H_2O + O=\overset{HO\ HO}{P}-O-\overset{HO\ HO}{P}=O.}$$

Pyrophosphates are formed when monohydrogen orthophosphates are heated. Thus, by heating hydrogen disodium orthophosphate, sodium pyrophosphate is formed—

$$2HNa_2PO_4 - H_2O = Na_4P_2O_7.$$

When ammonium magnesium phosphate (see above) is heated in the same way, it loses water and ammonia, and is transformed into magnesium pyrophosphate, thus—

$$2(NH_4)MgPO_4 = Mg_2P_2O_7 + H_2O + 2NH_4.$$

**Properties.**—Pyrophosphoric acid is an opaque white crystalline solid, readily soluble in water. Its aqueous solution passes slowly into orthophosphoric acid, the change taking place rapidly on boiling; a solution of this acid therefore cannot be concentrated by boiling.

The pyrophosphates are stable salts, and their solutions may be boiled without change; by boiling with acids, however, they are converted into orthophosphates.

**Metaphosphoric Acid,** $HPO_3$ or $PO_2(HO)$.—This acid is formed when phosphorus pentoxide is allowed to deliquesce. It may be obtained by the abstraction of one molecule of water from one molecule of orthophosphoric acid, which is brought about by heating the tribasic acid to redness—

$$H_3PO_4 - H_2O = HPO_3.$$

It is also obtained by strongly heating pyrophosphoric acid—

$$H_4P_2O_7 - H_2O = 2HPO_3.$$

The sodium salt is obtained by strongly igniting either dihydrogen sodium phosphate, $H_2NaPO_4$, or hydrogen sodium ammonium phosphate (*microcosmic salt*), $HNa(NH_4)PO_4$; or dihydrogen sodium pyrophosphate, $H_2Na_2P_2O_7$.

**Properties.**—Metaphosphoric acid is a transparent vitreous solid (frequently termed *glacial phosphoric acid*). It is readily fusible, and is usually cast into sticks. At a high temperature it may be volatilised. Metaphosphoric acid is easily soluble in water, and its solution is slowly transformed into orthophosphoric acid: this change takes place rapidly on boiling, and the acid passes directly into the tribasic acid without the intermediate formation of pyrophosphoric acid—

$$HPO_3 + H_2O = H_3PO_4.$$

Metaphosphoric acid is monobasic, but it possesses the remarkable property of forming a number of salts, which may be regarded as derived from several hypothetical polymeric varieties of the acid.

Monometaphosphoric acid, $HPO_3$, forms monometaphosphates, $NaPO_3$.
Dimetaphosphoric acid, $(HPO_3)_2$, ,, dimetaphosphates, $K_2P_2O_6$.
Trimetaphosphoric acid, $(HPO_3)_3$, ,, trimetaphosphates, $Na_3P_3O_9$.
Tetrametaphosphoric acid, $(HPO_3)_4$, ,, tetrametaphosphates, $Pb_2P_4O_{12}$.
Hexametaphosphoric acid, $(HPO_3)_6$, ,, hexametaphosphates, $Na_6P_6O_{18}$.

The three compounds, ortho-, pyro-, and metaphosphoric acids, are readily distinguished from each other by means of silver nitrate, and their action upon albumen :—

| Reagent. | Orthophosphoric Acid. | Pyrophosphoric Acid. | Metaphosphoric Acid. |
|---|---|---|---|
| Silver nitrate. | Canary yellow precipitate of $Ag_3PO_4$ | White crystalline precipitate of $Ag_4P_6O_7$ | White gelatinous precipitate of $AgPO_3$ |
| Albumen . . | No action | No action | Coagulates |

Orthophosphoric acid is also distinguished by giving a yellow precipitate of ammonium phospho-molybdate, upon the addition of excess of a solution of ammonium molybdate in nitric acid (see Molybdenum).

**Compounds of Phosphorus containing Nitrogen.**—By the action of ammonia upon phosphorus pentachloride, and upon phosphoryl chloride ($POCl_3$), a number of nitrogen derivatives are obtained. Thus, when gaseous ammonia is passed over phosphorus pentachloride, and the solid mass so obtained is heated in a stream of an inert gas, until the ammonium chloride is driven off, a white insoluble powder remains, having the composition represented by the formula PN(NH), to which the name *phospham* has been given—

$$PCl_5 + 7NH_3 = 5NH_4Cl + PN(NH).$$

**Phosphoryl Triamide,** $PO(NH_2)_3$, is obtained by the action of gaseous ammonia upon phosphoryl chloride—

$$POCl_3 + 6NH_3 = PO(NH_2)_3 + 3NH_4Cl.$$

When heated out of contact with air, phosphoryl triamide yields ammonia and *phosphoryl nitride*, thus—

$$PO(NH_2)_3 = 2NH_3 + PON.$$

**Pyrophosphamic Acids.**—Three of these compounds are known, which may be regarded as pyrophosphoric acid, in which 1, 2, and 3 of the (HO) groups have been replaced respectively by the group ($NH_2$), thus—

| | |
|---|---|
| Pyrophosphoric acid | $P_2O_3(HO)_4$. |
| Pyrophosphamic acid | $P_2O_3(HO)_3(NH_2)$. |
| Pyrophosphodiamic acid | $P_2O_3(HO)_2(NH_2)_2$. |
| Pyrophosphotriamic acid | $P_2O_3(HO)(NH_2)_3$. |

**Compounds of Phosphorus with Sulphur.**—A number of compounds of phosphorus and sulphur have been obtained by heating together varying proportions of sulphur and red phosphorus. The following compounds are known:—

| | | Analogous Oxides. |
|---|---|---|
| Phosphorus monosulphide | $P_4S$ | $P_4O$. |
| Phosphorus sesquisulphide | $P_4S_3$ | — |
| Phosphorus trisulphide | $P_2S_3$ | $P_4O_6$. |
| Phosphorus tetrasulphide (?) | $P_2S_4$ | $P_2O_4$. |
| Phosphorus pentasulphide | $P_2S_5$ | $P_2O_5$. |

**Phosphorus Pentasulphide,** $P_2S_5$.—This compound is the best-known member of the series. It is prepared by gently heating red phosphorus and fragments of sulphur, in the proportion required by the formula, in a flask. The elements combine with energy, and on cooling, a solid mass is obtained. This solid material is then distilled in a current of carbon dioxide, when the pentasulphide is obtained in the form of yellow crystals. The compound may also be obtained by dissolving ordinary phosphorus and sulphur in the proper proportions in carbon disulphide, and heating the solution in sealed tubes to 210°. On allowing the solution to cool, yellow crystals of the pentasulphide are deposited. Phosphorus pentasulphide is decomposed by water with the formation of orthophosphoric acid and the evolution of sulphuretted hydrogen—

$$P_2S_5 + 8H_2O = 2H_3PO_4 + 5H_2S.$$

## ARSENIC.

Symbol, As. Atomic weight = 74.9. Molecular weight = 299.6.
Vapour density = 149.8.

**Occurrence.**—Arsenic is found in the free state in nature, usually in the form of small nodules, more rarely as distinct crystals. In combination with sulphur it constitutes the minerals *realgar*, or *ruby sulphur*, $As_2S_2$; and *orpiment*, $As_2S_3$. In combination with metals, as arsenides, it occurs widely distributed, the commonest ores being *arsenical iron*, $FeAs_2$ and $Fe_4As_3$; *kupfernickel*, NiAs and $NiAs_2$; and *tin white cobalt*, $CoAs_2$. With metals and sulphur, it is met with in such minerals as *arsenical pyrites*, *mispickel*, or *white mundic*, $FeS_2,FeAs_2$; *cobalt glance*, $CoS_2,CoAs_2$; *nickel glance*, $NiS_2$, $NiAs_2$. Arsenic is present in small quantities in most samples of iron pyrites, hence it finds its way into sulphuric acid manufactured from pyrites. It also occurs in coal smoke, being derived from the pyrites contained in coal, and hence is present in the atmosphere: during the prevalence of yellow fogs the amount of arsenic present is very appreciable.

**Modes of Formation.**—On the small scale, arsenic is obtained by heating a mixture of arsenious oxide, $As_4O_6$, with powdered charcoal—

$$As_4O_6 + 6C = 6CO + 4As.$$

On a larger scale it is usually obtained either from native arsenic or from arsenical pyrites; the latter substance, when heated, gives up arsenic, and ferrous sulphide is left behind—

$$FeS_2,FeAs_2 = 2As + 2FeS.$$

The mineral is heated in long narrow horizontal earthenware retorts, into whose mouths are fitted earthenware receivers. The arsenic volatilises, and condenses in these receivers as a compact crystalline solid. It is purified by redistillation.

**Properties.**—Arsenic which has been resublimed, is a brilliant steel-grey metallic-looking substance, forming hexagonal rhombohedral crystals, having a specific gravity of 5.62 to 5.96. It is very brittle, and is a good conductor of heat and electricity. Arsenic begins to volatilise at 100°, and rapidly vaporises at a dark-red heat, passing from the solid to the vaporous states without liquefying. The vapour has a yellow colour and an unpleasant garlic smell. When heated under pressure, arsenic melts at 500°, and on cooling, solidifies to a compact crystalline mass. When arsenic is vaporised in a glass tube, in a current of hydrogen, it condenses along the tube in three distinct conditions: that which is deposited nearest to the heated portion of the tube is in the form of rhombohedral crystals; that which sublimes a little farther along, and condenses at a point where the temperature is about 210–220°, consists of a black shining amorphous deposit, while at a still more distant and cooler portion of the tube, a grey crystalline sublimate is formed. These are regarded as allotropic modifications of arsenic. The amorphous variety is also formed, when arsenuretted hydrogen is decomposed by being passed through a heated tube (*q.v.*). Amorphous arsenic is unacted upon by air at ordinary temperatures, and only slightly oxidised at 80°. The grey crystalline variety is readily oxidised on exposure to air at ordinary temperatures.

Amorphous arsenic, when heated out of contact with air to 360°, is converted into the rhombohedral variety.

Arsenic, like phosphorus, forms tetratomic molecules, its molecular weight as deduced from its vapour density being $74.9 \times 4 = 299.6$.

When heated in oxygen, arsenic burns with a bright bluish-white flame, forming arsenious oxide, $As_4O_6$. It is oxidised by sulphuric acid, nitric acid, and other oxidising agents. It combines readily with chlorine, and when thrown into this gas in the condition of powder it spontaneously inflames, forming arsenic trichloride. Thrown into bromine, a fragment of arsenic spontaneously inflames, and burns as it floats about upon the surface of the liquid.

Arsenic, in many of its characteristics, resembles the true metals: it is one of those elements lying on the borderland between true metals and non-metals, to which the name *metalloid* is applied. It is capable of forming alloys with metals, and an alloy of this element with lead, is employed for the manufacture of shot. It is found that by the addition of a small proportion of arsenic to lead, the melted metal is more fluid, and therefore more readily assumes the spheroidal form when projected from the *shot tower*, and on solidification the alloy is considerably harder than pure lead.

**ARSENURETTED HYDROGEN** (*Arsenic trihydride. Arsine*).

Formula, $AsH_3$. Molecular weight = 77.9. Density = 38.95.

**Modes of Formation.**—(1.) Arsenuretted hydrogen is formed when soluble arsenic compounds are exposed to the action of nascent hydrogen: thus, when a solution of arsenious oxide is introduced into a mixture from which hydrogen is being generated, such as zinc or iron and dilute hydrochloric or sulphuric acid, arsenic trihydride is obtained, mixed with free hydrogen—

$$As_4O_6 + 12H_2 = 4AsH_3 + 6H_2O.$$

(2.) By the same action of nascent hydrogen, arsenic trihydride is formed when a solution of either arsenious oxide, $As_4O_6$, or arsenic oxide, $As_2O_5$, is subjected to electrolysis.

(3.) Arsenic trihydride is also formed, when arsenical compounds are in contact with organic matter which is undergoing decomposition. During the growth of certain moulds and fungi a small quantity of hydrogen is evolved, which by its action upon the arsenic compound, gives rise to the formation of arsenic trihydride. By this action arsenic trihydride is sometimes formed in dwelling-houses where arsenical wall-papers are employed, and where, from dampness or other causes, mould develops.

(4.) Pure arsenic trihydride is prepared by the action of dilute hydrochloric or sulphuric acid upon an alloy of arsenic and zinc—

$$As_2Zn_3 + 3H_2SO_4 = 2AsH_3 + 3ZnSO_4,$$

or by the action of either water or dilute acid upon an alloy of arsenic and sodium, prepared by heating sodium in the impure arsenic trihydride obtained by method No. 1.

**Properties.**—Arsenic trihydride is a colourless, offensive-smelling, and highly poisonous gas. Under pressure it condenses to a colourless liquid, which boils at −54.8° and solidifies at −113.5°. The gas burns with a lilac-coloured flame, forming water and white fumes of arsenious oxide—

$$4AsH_3 + 6O_2 = As_4O_6 + 6H_2O.$$

When the supply of air to the flame is limited, as when a cold surface is depressed upon it, water is formed and arsenic is deposited as a shining black amorphous film—

$$4AsH_3 + 3O_2 = As_4 + 6H_2O.$$

Arsenuretted hydrogen is readily decomposed by heat into its elements: thus, when the gas is passed through a glass tube, which is heated at one point by a Bunsen flame, arsenic in the amorphous condition is deposited upon the tube immediately beyond the heated spot. Even when greatly diluted with hydrogen this reaction takes place, and it therefore affords a delicate test for the presence of exceedingly small quantities of arsenic. This method for the detection of arsenical compounds is known as *Marsh's test*, and may be carried out by means of the apparatus seen in Fig. 121. Hydrogen is generated in the two-necked bottle from zinc and dilute sulphuric acid (which are themselves free from arsenic), and the arsenic in the form of an oxygen or a haloid compound is introduced. On igniting the issuing gas, and depressing a white porcelain capsule into the flame, black stains of amorphous arsenic are produced: and if the tube be heated as shown in the figure, the arsenic is deposited as a black film. The corresponding antimony compound, $SbH_3$ (*q.v.*), gives rise to a similar deposit of metallic antimony, when treated in the same way; but the arsenic deposit is readily distinguished by being easily soluble in a solution of calcium hypochlorite. Many metals, such as sodium, or potassium, when heated in arsenuretted hydrogen, form alloys with the arsenic, and hydrogen is set at liberty; while metallic oxides when similarly treated form metallic arsenides and water.

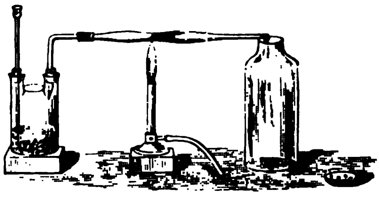


FIG. 121.

Arsenuretted hydrogen is slightly soluble in water, but the solution on exposure to air deposits arsenic.

When passed into a solution of silver nitrate, metallic silver is precipitated, and a solution of arsenious oxide (the hypothetical arsenious acid, $H_3AsO_3$) is obtained, thus—

$$AsH_3 + 6AgNO_3 + 3H_2O = 3Ag_2 + 6HNO_3 + H_3AsO_3.$$

When the gas is passed into copper sulphate solution, cuprous arsenide is precipitated—

$$2AsH_3 + 3CuSO_4 = 3H_2SO_4 + As_2Cu_3.$$

Arsenuretted hydrogen is decomposed by the halogens with energy, forming the haloid compound of arsenic, and the halogen acid—

$$AsH_3 + 3Cl_2 = AsCl_3 + 3HCl.$$

**Solid Arsenuretted Hydrogen.**—When arsenide of potassium or sodium is acted upon by water, a soft brown solid substance separates, which contains equal atomic proportions of arsenic and hydrogen. Its molecular weight is unknown, its composition is therefore expressed by the formula, $(AsH)_n$.

### *COMPOUNDS OF ARSENIC WITH THE HALOGENS.*

The following compounds are known—

$$AsF_3; \quad AsCl_3; \quad AsBr_3; \quad AsI_3.$$

Two other compounds with iodine have been described, containing the elements in the proportion represented by the formulæ, $AsI_2$ and $As_2I_6$, the molecular weights of which are unknown.

**Arsenic Fluoride,** $AsF_3$; molecular weight = 131.9, is formed when sodium fluoride is heated with arsenic chloride—

$$3NaF + AsCl_3 = 3NaCl + AsF_3.$$

It is best obtained by distilling a mixture of arsenious oxide, powdered fluor spar, and sulphuric acid in a leaden retort. The hydrofluoric acid generated by the action of the acid upon the calcium fluoride, reacts upon the arsenious oxide, thus—

$$As_4O_6 + 12HF = 4AsF_3 + 6H_2O.$$

**Properties.**—Arsenic fluoride is a colourless fuming liquid, boiling at 60.4°. It is rapidly decomposed by water into arsenious oxide and hydrofluoric acid. On this account it forms painful wounds when brought into contact with the skin.

**Arsenic Chloride,** $AsCl_3$; molecular weight = 181.11, is obtained when arsenic burns in chlorine, or when chlorine is passed over fragments of arsenic in a tube.

It is also produced when either arsenic or arsenious sulphide is distilled with mercuric chloride—

$$2As + 6HgCl_2 = 3Hg_2Cl_2 + 2AsCl_3.$$
$$As_2S_3 + 3HgCl_2 = 3HgS \quad + 2AsCl_3.$$

It is readily prepared by the action of hydrochloric acid upon arsenious oxide; for which purpose sodium chloride, arsenious oxide, and sulphuric acid are gently heated together in a retort connected with a well-cooled receiver—

$$As_4O_6 + 12HCl = 4AsCl_3 + 6H_2O.$$

**Properties.**—Arsenic chloride is a colourless, fuming, and somewhat oily liquid, which boils at 130.2°, and is extremely poisonous. In the presence of excess of water, or when added to warm water, it is decomposed into arsenious oxide and hydrochloric acid. With a small quantity of water a solid crystalline arsenic chlorhydroxide is formed, $As(HO)_2Cl$—

$$AsCl_3 + 2H_2O = 2HCl + As(HO)_2Cl.$$

**Arsenious Bromide,** $AsBr_3$.—This compound is formed by the direct union of arsenic with bromine, and is prepared by adding powdered arsenic to a solution of bromine in carbon disulphide. On evaporation, the compound is deposited in the form of colourless deliquescent crystals, which melt at 20° to 25° to a straw-coloured liquid.

**Arsenious Iodide,** $AsI_3$, is obtained by heating a mixture of arsenic and iodine. It is most conveniently prepared by digesting a saturated ethereal solution of iodine, with powdered arsenic, in a flask with a reflux condenser. On filtering and cooling, the iodide deposits in the form of lustrous red hexagonal crystals.

## *OXIDES AND OXYACIDS OF ARSENIC.*

Two oxides of arsenic are known, both of which act as anhydrides—

| | |
|---|---|
| Arsenious oxide | $As_4O_6$. |
| Arsenic oxide (arsenic pentoxide) | $As_2O_5$. |

No acid corresponding to arsenious oxide is known in the free state, although the arsenites constitute a class of stable salts.

Three arsenic acids, derived from arsenic pentoxide, are known, analogous in constitution to the three phosphoric acids, namely—

| | |
|---|---|
| Ortho-arsenic acid . . . | $H_3AsO_4$ or $AsO(HO)_3$. |
| Pyro-arsenic acid . . . | $H_4As_2O_7$ or $As_2O_3(HO)_4$. |
| Metarsenic acid . . . | $HAsO_3$ or $AsO_2(HO)$. |

## ARSENIOUS OXIDE.

Formula, $As_4O_6$. Molecular weight = 395.36.

**Mode of Formation.**—Arsenious oxide is formed when arsenic burns in air or in oxygen, or when arsenic minerals are roasted in a current of air. On a small scale it may be produced by burning arsenic in a hard glass tube in a stream of oxygen, and allowing the white fumes of arsenious oxide to pass into a glass cylinder (as shown in Fig. 122), where the greater part condenses, while the rest is led into a draught flue.

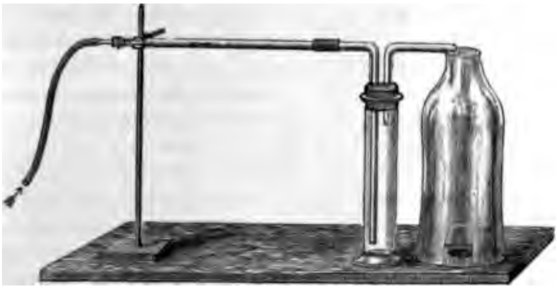


FIG. 122.

Arsenious oxide is obtained as a secondary product, in the metallurgical process of roasting arsenical ores of nickel, cobalt, tin, silver, and others, for the extraction of these metals. It is also obtained as a principal product by roasting arsenical pyrites. The ore is heated either upon the hearth of a reverberatory furnace, where it is raked over from time to time, or it is introduced by means of a *hopper*, into one end of a long clay-lined iron cylinder, placed at an incline of about 1 in 18, and caused slowly to revolve about its longitudinal axis, Fig. 123. The lower end of this cylinder enters a furnace, the upper end is connected to a series of brickwork flues. The ore is delivered into the upper end of the revolving cylinder, and as it gradually gravitates down the incline, it is completely roasted by the furnace flames which pass over it, and finally falls out into a chamber beneath. The fumes of arsenious oxide pass through a series of chambers or flues, so arranged as to present an extensive condensing surface to the gases, and the crude product, known as ***arsenical soot***, is from time to time collected. This is known as Oxland and Hocking's revolving calciner.

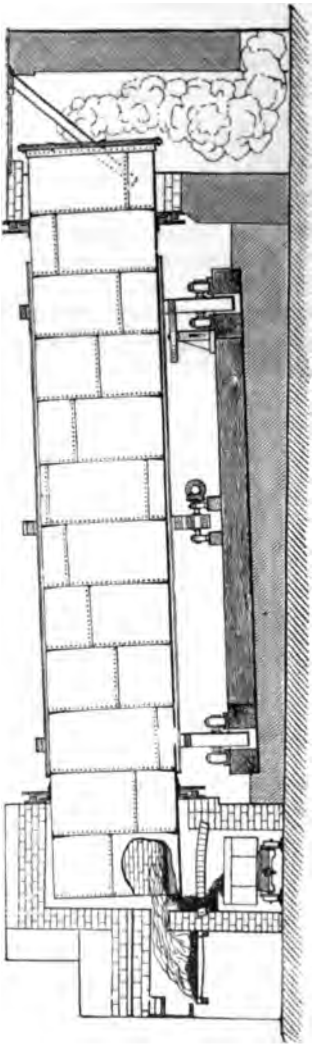


FIG. 123.

**Properties.**—Arsenious oxide, known familiarly as *white arsenic*, or simply *arsenic*, is known in three modifications—

(1.) Amorphous.
(2.) Octahedral crystals of the regular system.
(3.) Prismatic crystals of the trimetric system.

*Amorphous Arsenious Oxide* is a colourless, transparent, vitreous substance, which is obtained when the vapour of the oxide is condensed at a temperature only slightly below its vaporising point. On exposure, it gradually becomes opaque, being transformed into the regular octahedral variety. This change takes place from the outside, and lumps of opaque "white arsenic," when broken, often show a nucleus of the vitreous modification. Amorphous arsenious oxide may be preserved unchanged in sealed tubes. The change from the vitreous to the crystalline form is attended with evolution of heat, and a diminution of specific gravity from 3.738 to 3.689.

Amorphous arsenious oxide, when heated to about 200°, melts, and at a higher temperature vaporises. It is soluble in 108 parts of cold water.

*Octahedral Arsenious Oxide.*—The vitreous form passes spontaneously into this variety. It is obtained directly, by quickly cooling the vapour of arsenious oxide, or by crystallisation from the aqueous solution of either form of the oxide. Arsenious oxide is also deposited in this form from solution in hydrochloric acid.

Octahedral arsenious oxide is less soluble in water than the amorphous variety, 1 part requiring 355 parts of water for its solution. When heated, the crystals vaporise without fusion, but when heated under pressure they melt, and are converted into the vitreous form.

*Prismatic Arsenious Oxide* is obtained by crystallisation from a hot saturated solution of arsenious oxide in potassium hydroxide.

Aqueous solutions of arsenious oxide possess a feeble acid reaction, probably due to the formation of unstable arsenious acid, $H_3AsO_3$. The acid has not been isolated, and on concentration the solution deposits crystals of arsenious oxide.

Arsenious oxide is a powerful poison: from 2 to 4 grains usually prove fatal. It is possible, however, by the habitual use of it, to so accustom the system to this poison, that doses sufficiently large to cause certain death to one unused to it, may be taken with apparent impunity. The use of arsenic is said to beautify the complexion, and to improve the wind. The men who are employed upon arsenic works, are constantly liable to swallow doses of arsenious oxide which would cause death to one unaccustomed to the occupation.

**Arsenites.**—Three classes of arsenites are known, which may be regarded as being derived from the three hypothetical acids—

| | | |
|---|---|---|
| Ortho-arsenious acid, $H_3AsO_3$, or $As(HO)_3$ | Silver ortho-arsenite, | $Ag_3AsO_3$. |
| | Hydrogen copper arsenite (Scheele's green), | $HCuAsO_3$. |
| Pyro-arsenious acid, $H_4As_2O_5$, or $As_2O(HO)_4$ | Calcium pyro-arsenite, | $Ca_2As_2O_3$. |
| | Barium pyro-arsenite, | $Ba_2As_2O_5$. |
| | Ammonium pyro-arsenite, | $(NH_4)_4As_2O_5$. |

Metarsenious acid, $HAsO_2$, or $AsO(HO)$ $\left\{\begin{array}{l}\text{Potassium metarsenite, } KAsO_2.\\ \left.\begin{array}{l}\text{Acid potassium}\\ \text{metarsenite,}\end{array}\right\} KAsO_2,HAsO_2\\ \text{Lead metarsenite, } Pb(AsO_2)_2.\end{array}\right.$

The pigment known as *Schweinfurt green*, is a double metarsenite and acetate of copper—

$$3Cu(AsO_2)_2,Cu(C_2H_3O_2)_2.$$

All arsenites, except those of the alkali metals, are insoluble in water. When heated, most arsenites are converted into *arsenates* and arsenic; and when heated with charcoal the whole of the arsenic is reduced.

**Arsenic Pentoxide,** $As_2O_5$.—This oxide is not formed when arsenic burns in oxygen. It is obtained by the oxidation of arsenious oxide by nitric acid, and subsequently heating the arsenic acid so produced, to a dark-red heat—

$$2H_3AsO_4 = 3H_2O + As_2O_5.$$

**Properties.**—Arsenic pentoxide is a white deliquescent solid, completely soluble in water, with the formation of arsenic acid.

When strongly heated it breaks up into arsenious oxide and oxygen—

$$2As_2O_5 = As_4O_6 + 2O_2.$$

### *ARSENIC ACIDS AND ARSENATES.*

When arsenic pentoxide is dissolved in water, crystals are obtained having the composition $2AsO(HO)_3,H_2O$. At 100° these melt and lose water, leaving ortho-arsenic acid, $H_3AsO_4$. By the withdrawal of water from this acid, both pyro- and metarsenic acids are obtained.

Heated between 140° and 180°, two molecules of the "ortho" acid lose one of water—

$$2H_3AsO_4 = H_4As_2O_7 + H_2O.$$

And by heating the pyro-arsenic acid so obtained to 200°, another molecule of water is expelled, with the formation of metarsenic acid (*compare corresponding acids of phosphorus*)—

$$H_4As_2O_7 = 2HAsO_3 + H_2O.$$

Pyro- and metarsenic acids are both crystalline solids, which ssolve in water with the evolution of heat and formation of ortho-senic acid; aqueous solutions of these two acids, therefore, nnot exist. In this respect they differ from the corresponding osphorus acids, both of which can be obtained in aqueous lution.

Each of the three arsenic acids forms salts, of which the following e examples:—

| | |
|---|---|
| Trisodium ortho-arsenate . . . | $Na_3AsO_4$. |
| Hydrogen disodium ortho-arsenate . | $HNa_2AsO_4$. |
| Dihydrogen sodium ortho-arsenate . | $H_2NaAsO_4$. |
| Ammonium magnesium ortho-arsenate . | $(NH_4)MgAsO_4$. |
| Sodium pyro-arsenate . . . . | $Na_4As_2O_7$. |
| Sodium metarsenate . . . . | $NaAsO_3$. |

The salts of pyro- and metarsenic acids, like the acids themlves, only exist in the solid state; when dissolved in water they ss into the ortho-compounds.

The arsenates are isomorphous with the corresponding phosates.

## COMPOUNDS OF ARSENIC WITH SULPHUR.

Three sulphides of arsenic are known, namely—

| | |
|---|---|
| Arsenic disulphide (*found native as Realgar*) . | $As_2S_2$. |
| Arsenic trisulphide (*found native as Orpiment*) . | $As_2S_3$. |
| Arsenic pentasulphide . . . . . . . | $As_2S_5$. |

**Arsenic Disulphide,** $As_2S_2$, is formed when sulphur and arsenic, arsenic trisulphide and arsenic, are heated together; or by eating arsenious oxide and sulphur—

$$As_4O_6 + 7S = 2As_2S_2 + 3SO_2.$$

It is prepared on a large scale by distilling a mixture of iron yrites and arsenical pyrites—

$$FeS_2,FeAs_2 + 2FeS_2 = As_2S_2 + 4FeS.$$

**Properties.**—Arsenic disulphide is a red, vitreous, brittle solid, aving a specific gravity of 3.5. It is readily fusible, and sublimes nchanged. Heated in air or oxygen, it burns with a blue flame, rming arsenious oxide and sulphur dioxide—

$$2As_2S_2 + 7O_2 = 4SO_2 + As_4O_6.$$

Arsenic disulphide is employed in pyrotechny. So-called *Bengal fire* consists of a mixture of realgar, sulphur, and nitre.

**Arsenic Trisulphide,** $As_2S_3$, is obtained by heating sulphur and arsenic in the proportion required by the formula, and subliming the compound.

It may readily be produced by passing sulphuretted hydrogen through a solution of arsenious oxide in hydrochloric acid—

$$As_4O_6 + 6H_2S = 2As_2S_3 + 6H_2O.$$

**Properties.**—The compound, as obtained by precipitation with sulphuretted hydrogen, is a pure canary-yellow solid, which easily melts, and on again cooling forms a brittle crystalline mass. It volatilises and sublimes unchanged, but when heated in air or oxygen it burns with formation of arsenious oxide and sulphur dioxide.

Arsenic trisulphide may be regarded as a thio-anhydride, as it gives rise to a series of salts known as *thio-arsenites*, or *sulpharsenites*. Thus, when arsenic trisulphide is brought into a solution of a caustic alkali, such as potassium hydroxide, the sulphide readily dissolves with the formation of an arsenite and thioarsenite, thus—

$$As_2S_3 + 4KHO = HK_2AsO_3 + HK_2AsS_3 + H_2O.$$

Upon the addition of an acid, the salts are decomposed and arsenic trisulphide reprecipitated—

$$HK_2AsO_3 + HK_2AsS_3 + 4HCl = 4KCl + 3H_2O + As_2S_3.$$

**Thio-arsenites.**—These salts may be looked upon as being derived from three hypothetical thio-arsenious acids, corresponding to the oxyacids—

| | |
|---|---|
| Ortho-thio-arsenious acid, $H_3AsS_3$. | Potassium ortho-thio-arsenite, $K_3AsS_3$. |
| Pyro-thio-arsenious acid, $H_4As_2S_5$. | Ammonium pyro-thio-arsenite, $(NH_4)_4As_2S_5$.<br>Lead pyro-thio-arsenite, $Pb_2As_2O_5$. |
| Meta-thio-arsenious acid, $HAsS_2$. | Potassium meta-thio-arsenite, $KAsS_2$. |

Thio-arsenites of the alkali metals, the metals of the alkaline earths, and of magnesium, are soluble in water, but decompose on boiling. Their solutions are decomposed by acids, with evolution of sulphuretted hydrogen and precipitation of arsenic trisulphide, thus—

$$2K_3AsS_3 + 6HCl = 6KCl + 3H_2S + As_2S_3.$$

**Arsenic Pentasulphide,** $As_2S_5$.—This compound is prepared by adding an acid to a solution of a thio-arsenate, thus—

$$2Na_3AsS_4 + 6HCl = 6NaCl + 3H_2S + As_2S_5.$$

Arsenic pentasulphide is a yellow, easily fusible solid. It is readily soluble in caustic alkalies, forming an arsenate and a thioarsenate—

$$As_2S_5 + 4KHO = HK_2AsO_4 + HK_2AsS_4 + H_2O.$$

Arsenic pentasulphide, like the trisulphide, gives rise to a series of salts, known as thio-arsenates. These may be regarded as being derived from the three hypothetical thio-arsenic acids—

| | |
|---|---|
| Ortho-thio-arsenic acid, $H_3AsS_4$. | Tripotassium ortho-thio-arsenate, $K_3AsS_4$.<br>Hydrogen disodium ortho-thio-arsenate, $HNa_2AsS_4$. |
| Pyro-thio-arsenic acid, $H_4As_2S_7$. | Magnesium pyro-thio-arsenate, $Mg_2As_2S_7$. |
| Meta-thio-arsenic acid, $HAsS_3$. | Ammonium meta-thio-arsenate, $(NH_4)AsS_3$. |

## ANTIMONY.

Symbol, Sb. Atomic weight = 119.6.

**Occurrence.**—Antimony in the uncombined state is found in small quantities in various parts of the world, and notably in Borneo. In combination with oxygen, as $Sb_2O_3$, it constitutes the mineral *antimony bloom*, or *white antimony;* and as $Sb_2O_4$ it occurs in *antimony ochre.* In combination with sulphur, as $Sb_2S_3$, it occurs as the mineral *stibnite*, or *grey antimony ore*, which is the most important source of the metal; and with both oxygen and sulphur, as $Sb_2O_3,2Sb_2S_3$, it constitutes the mineral *antimony blende*, or *red antimony.*

It also occurs in combination with sulphur and with metals, in the form of *thio-antimonites.*

**Modes of Formation.**—(1.) Antimony is obtained from the native sulphide by one of the two following methods. The broken-up ore is heated in plumbago crucibles, along with scrap iron. As the mass melts, the sulphur combines with the iron, forming a slag of iron sulphide, and the liberated antimony settles out beneath—

$$Sb_2S_3 + 3Fe = 2Sb + 3FeS.$$

(2.) The crude sulphide is first *liquated*, or melted in such a manner as to separate the sulphide from the rocky matter associated with it. The liquated sulphide is then mixed with about half its weight of charcoal, in order to prevent the mass from caking, and carefully roasted. During this process, the antimony sulphide is partially converted into antimony trioxide ($(Sb_2O_3)_2$), which passes into flues, and is there condensed, leaving a mixture containing antimony tetroxide ($Sb_2O_4$), and unchanged sulphide. Most of the arsenic present is also oxidised, and volatilises with the antimony trioxide, while sulphur dioxide escapes. The residue, consisting of the tetroxide and sulphide (known as antimony ash), is mixed with an additional quantity of charcoal and with sodium carbonate, and heated to redness in a crucible, when the changes represented by the following equations take place—

$$(1.)\quad Sb_2O_4 + 4C = 4CO + 2Sb.$$

By the action of the carbon upon the sodium carbonate, sodium is liberated, which combines with the sulphur of the trisulphide, forming sodium sulphide and metallic antimony—

$$(2.)\quad Na_2CO_3 + 2C = 3CO + 2Na.$$

$$(3.)\quad Sb_2S_3 + 3Na_2 = 3Na_2S + 2Sb.$$

The sodium sulphide in its turn unites with a further quantity of antimony sulphide, forming a double sulphide of sodium and antimony, which, mixed with the sodium carbonate and charcoal, constitutes the slag. The metal obtained by either process is subsequently *refined.*

**Properties.**—Antimony is a bright, highly crystalline, and very brittle metal, possessing a bluish-white colour, and having a specific gravity of 6.7 to 6.8. It is unacted upon by air or oxygen at the ordinary temperature, but when heated it burns brilliantly, forming antimony trioxide. The metal melts at 450° ; and when allowed to solidify, its crystalline character is seen by the fern-like appearance of its surface. If a quantity of the molten metal be allowed slowly to cool, and when partially solidified the remaining liquid portion be poured off, the interior of the mass is found to be lined with well-formed rhombohedral crystals, isomorphous with arsenic. In the act of solidification antimony expands, a property which it imparts to its alloys, thus giving to them the valuable quality of taking very fine and sharp castings. The most important of these alloys are *type metal* (lead 75, antimony 20, tin 5) ; *stereotype metal* (lead 112, antimony 18, tin 3) ; *Britannia metal* (tin 140, copper 3, antimony 9). Regarded as a metal, antimony is a bad conductor of heat and electricity.

Dilute sulphuric and hydrochloric acids are without action upon antimony. The concentrated acids convert it into sulphate and chloride respectively—

$$2Sb + 6H_2SO_4 = 3SO_2 + 6H_2O + Sb_2(SO_4)_3.$$

Antimony is oxidised by nitric acid, dilute acid converting it into antimony trioxide, or a compound of the oxide with nitrogen pentoxide, $Sb_2O_3,3N_2O_5$, while strong acid oxidises it chiefly into antimony tetroxide and pentoxide.

Powdered antimony, when thrown into chlorine, takes fire spontaneously, and forms antimony trichloride.

**Amorphous Antimony.**—Antimony is obtained in an amorphous form, by the electrolysis of a solution of tartar emetic in antimony trichloride.

**Properties.**—Amorphous antimony presents the appearance of a smooth polished rod of graphite, and has a specific gravity of 5.78. It always contains a certain quantity of antimony trichloride (from 4 to 12 per cent.); but whether this is in chemical union, or merely mechanically retained by the metal, is not known. Amorphous antimony is very unstable, and readily passes into the crystalline modification: a slight blow, even a scratch with a needle, causes it instantly to transform itself into the stable form, with explosive violence; the temperature at the same moment rising to 250°, and clouds of the vapour of antimony trichloride being evolved.

## ANTIMONY HYDRIDE (*Antimoniuretted Hydrogen*).

Symbol, $SbH_3$.

**Modes of Formation.**—(1.) This compound has never been obtained in the pure state, as usually prepared it is always mixed with hydrogen. It is formed when a solution of antimony trichloride in hydrochloric acid is introduced into a mixture generating hydrogen, such as zinc and sulphuric acid.

(2.) It is also found by the action of dilute sulphuric acid upon alloys of antimony and zinc—

$$Sb_2Zn_3 + 3H_2SO_4 = 3ZnSO_4 + 2SbH_3.$$

**Properties.**—Antimony hydride is a colourless, offensive-smelling, and poisonous gas, closely resembling the corresponding arsenic compound in its general behaviour. It burns with a violet-tinted flame, forming water and antimony trioxide—

$$4SbH_3 + 6O_2 = 6H_2O + Sb_4O_6.$$

When the supply of air is limited, water is formed and antimony is deposited; when, therefore, a cold object is depressed upon the flame, black stains of metallic antimony are obtained. The gas is easily decomposed by heat, and if passed through a glass tube heated at one point, a black deposit of antimony is formed upon the glass. The antimony so deposited is insoluble in a solution of bleaching powder (see Arsenic Hydride). Antimony hydride is decomposed by the halogen elements, with the formation of the halogen hydride, and the halogen compound of antimony—

$$SbH_3 + 3Cl_2 = 3HCl + SbCl_3.$$

Sulphuretted hydrogen, under the influence of sunshine, converts antimony hydride into antimony trisulphide—

$$2SbH_3 + 3H_2S = Sb_2S_3 + 6H_2.$$

When passed into silver nitrate solution, the antimony is precipitated in combination with silver, in this way differing from the arsenic analogue—

$$SbH_3 + 3AgNO_3 = 3HNO_3 + SbAg_3.$$

## *COMPOUNDS OF ANTIMONY WITH THE HALOGENS.*

The compounds represented by the following formulæ are known—

$SbF_3$; $SbCl_3$; $SbBr_3$; $SbI_3$.
$SbF_5$; $SbCl_5$.

**Antimony Trifluoride**, $SbF_3$, is prepared by dissolving the trioxide in aqueous hydrofluoric acid. From the concentrated solution it is deposited in the form of white deliquescent crystals. It dissolves in water, and is gradually converted into an oxyfluoride.

**Antimony Pentafluoride**, $SbF_5$, is obtained when hydrated antimony pentoxide is dissolved in aqueous hydrofluoric acid. When the solution is evaporated the compound remains as an amorphous gum-like residue.

Both of these fluorides exhibit a great tendency to unite with alkaline fluorides, forming double salts, such as $SbF_3,2KF$; $SbF_3 2NH_4F$, in the case of the trifluoride; and $SbF_5,KF$; $SbF_5,2KF$, with the pentafluoride.

**Antimony Trichloride,** $SbCl_3$, is formed when chlorine is passed over metallic antimony, or antimony trisulphide—

$$2Sb + 3Cl_2 = 2SbCl_3.$$
$$2Sb_2S_3 + 9Cl_2 = 4SbCl_3 + 3S_2Cl_2.$$

It may also be obtained by the action of boiling hydrochloric acid, containing a small quantity of nitric acid, upon either metallic antimony, antimony trioxide, or trisulphide—

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

**Properties.**—Antimony trichloride is a colourless, deliquescent, crystalline substance, melting at 73.2° to an oily liquid, which again solidifies to a soft translucent mass. It is soluble in alcohol and in carbon disulphide, and from the latter may be crystallised. It may be dissolved in a small quantity of water unchanged. Thus, if allowed to deliquesce it liquefies in the water it absorbs, forming a colourless solution, which, upon evaporation over sulphuric acid, again deposits crystals of the trichloride. The addition of larger quantities of water results in the formation of oxychlorides *—

$$(1.)\quad SbCl_3 + H_2O = 2HCl + SbOCl.$$
$$(2.)\quad 4SbCl_3 + 5H_2O = 10HCl + Sb_4O_5Cl_2.$$

Continued boiling with water removes the whole of the chlorine, forming the trioxide—

$$Sb_4O_5Cl_2 + H_2O = 2HCl + Sb_4O_6.$$

Antimony chloride unites with alkaline chlorides, forming double salts (see Antimony fluoride), such as $SbCl_3,2NH_4Cl$; $SbCl_3,3KCl$. With potassium bromide it forms the compound $SbCl_3,3KBr$, which, strangely enough, appears to be identical with the double compound of antimony tribromide with potassium chloride, $SbBr_3,3KCl$.

**Antimony Pentachloride,** $SbCl_5$, is obtained by passing excess of dry chlorine over metallic antimony, or antimony trichloride, in a retort, when antimony pentachloride distils over in the excess of chlorine—

---

* The mixed product obtained by the action of water upon antimony trichloride is known as *powder of Algaroth.*

$$SbCl_3 + Cl_2 = SbCl_5.$$

**Properties.**—Antimony pentachloride is a nearly colourless, strongly-fuming liquid. It solidifies, when cooled, to a mass of colourless crystals, which remelt at − 6°. Under the ordinary atmospheric pressure the pentachloride dissociates, when heated, into the trichloride and chlorine, but under reduced pressure it may be boiled and distilled. Thus, under a pressure of 22 mm. it boils at 79°.

By the regulated action of ice cold water, oxychlorides are formed—

(1.) $SbCl_5 + H_2O = SbOCl_3 + 2HCl.$
(2.) $SbOCl_3 + H_2O = SbO_2Cl + 2HCl.$

Antimony pentachloride, and also the oxychlorides, are converted by hot water into pyro-antimonic acid (analogous to pyro-arsenic and pyro-phosphoric acids)—

$$2SbCl_5 + 7H_2O = H_4Sb_2O_7 + 10HCl.$$
$$2SbO_2Cl + 3H_2O = H_4Sb_2O_7 + 2HCl.$$

Sulphuretted hydrogen (the sulphur analogue of water) acts upon antimony pentachloride, forming antimony sulphotrichloride, corresponding to the oxytrichloride—

$$SbCl_5 + H_2S = SbSCl_3 + 2HCl.$$

Antimony tribromide, $SbBr_3$, and antimony tri-iodide, $SbI_3$, are obtained by adding powdered antimony to solutions of the halogens in carbon disulphide, from which liquid the compounds are crystallised: the bromide as colourless deliquescent crystals, and the iodide as hexagonal ruby-red crystals. Both of these compounds are similarly acted upon by water, forming the oxybromides $SbOBr$; $Sb_4O_5Br_2$, and the oxyiodides $SbOI$; $Sb_4O_5I_2$.

## OXIDES AND OXYACIDS OF ANTIMONY.

Three oxides of antimony are known—

| | |
|---|---|
| Antimony trioxide (antimonious oxide) . | $(Sb_2O_3)_2$ or $Sb_4O_6$. |
| Antimony tetroxide . . . . | $Sb_2O_4$. |
| Antimony pentoxide . . . . | $Sb_2O_5$. |

No acids are known corresponding to the trioxide, although a sodium salt of the hypothetical metantimonious acid, $HSbO_2$, has been described, having the composition $NaSbO_2 . 3H_2O$.

Three acids are known derived from antimony pentoxide, which are analagous to the three arsenic and phosphoric acids—

| | |
|---|---|
| Orthoantimonic acid . . . . | $H_3SbO_4$. |
| Pyroantimonic acid . . . . . | $H_4Sb_2O_7$. |
| Metantimonic acid . . . . . | $HSbO_3$. |

**Antimony Trioxide,** $Sb_4O_6$, may be prepared by the addition of hot water to a solution of either antimony trichloride or antimony sulphate, and washing the precipitated oxide with a solution of sodium carbonate to remove the free acid—

$$4SbCl_3 + 12H_2O = 2Sb_4O_6 + 12HCl.$$

**Properties.**—Antimonious oxide is a white powder, which, when volatilised, condenses in two distinct forms, namely, prismatic crystals of the trimetric system, and regular octahedra. The former are deposited nearest to the heated material, the latter in more remote and cooler regions. (See *Arsenious Oxide, with which antimonious oxide is isodimorphous.*) Antimonious oxide is only very slightly soluble in water, and the solution is without action upon litmus. It is insoluble in nitric or sulphuric acid, but is dissolved by hydrochloric acid with formation of the trichloride. It is readily soluble in tartaric acid, and in a boiling solution of hydrogen potassium tartrate (*cream of tartar*), giving rise to potassium antimony tartrate, or *tartar emetic*—

$$4HK(C_4H_4O_6) + Sb_4O_6 = 4(SbO)K(C_4H_4O_6) + 2H_2O.$$

Antimonious oxide burns in the air, forming the tetroxide—

$$(Sb_2O_3)_2 + O_2 = 2Sb_2O_4.$$

**Antimony Tetroxide,** $Sb_2O_4$, is formed when the trioxide burns in air. It may be prepared by strongly heating antimony pentoxide—

$$2Sb_2O_5 = 2Sb_2O_4 + O_2$$

**Properties.**—Antimony tetroxide is a white non-volatile powder, which is insoluble in water. It is decomposed by boiling hydrogen potassium tartrate, forming tartar emetic and metantimonic acid, thus—

$$HK(C_4H_4O_6) + Sb_2O_4 = (SbO)K(C_4H_4O_6) + HSbO_3.$$

**Antimony Pentoxide,** $Sb_2O_5$, is obtained by oxidising metallic antimony with nitric acid, and heating the antimonic acid so obtained to a temperature not exceeding 275°.

**Properties.**—Antimony pentoxide is a straw-coloured powder, insoluble in water. When heated to 300°, it gives up oxygen and is converted into the tetroxide. Its feeble acidic character is seen by its formation of an alkaline metantimonate, when fused with an alkaline carbonate—

$$Sb_2O_5 + Na_2CO_3 = CO_2 + 2NaSbO_3.$$

**Antimonic Acids and Antimonates.**—None of the three antimonic acids can be obtained by the action of water upon the oxide. Pyro-antimonic acid is formed when antimony pentachloride is treated with hot water, and the precipitate dried at 100°—

$$2PCl_5 + 7H_2O = H_4Sb_2O_7 + 10HCl.$$

Pyro-antimonic acid readily passes, by loss of water, into metantimonic acid—

$$H_4Sb_2O_7 - H_2O = 2HSbO_3.$$

Metantimonic acid is also formed by oxidising metallic antimony by means of nitric acid—

$$2Sb + 4HNO_3 = 2HSbO_3 + NO_2 + 3NO + H_2O,$$

or by the decomposition of an aqueous solution of a metantimonate by means of nitric acid—

$$KSbO_3 + HNO_3 = KNO_3 + HSbO_3.$$

On allowing the precipitated metantimonic acid to remain for a long time in contact with water, it is converted into ortho-antimonic acid, $H_3SbO_4$—

$$HSbO_3 + H_2O = H_3SbO_4.$$

No salts of ortho-antimonic acid, $H_3SbO_4$, are known; the antimonates, therefore, belong to the two acids, pyro-antimonic acid and metantimonic acid—

| Pyro-antimonates.* | Metantimonates.* |
|---|---|
| Normal potassium pyro-antimonate, $K_4Sb_2O_7$. | Potassium metantimonate, $KSbO_3$. |
| Hydrogen potassium pyro-antimonate, $H_2K_2Sb_2O_7$. | Barium metantimonate, $Ba(SbO_3)_2$. |

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* As only two types of antimonates are known, and as the salts of the type, $MSbO_3$, are the best known, the name *antimonates* was formerly applied to

## *COMPOUNDS OF ANTIMONY WITH SULPHUR.*

'wo sulphides of antimony are known, namely—

| | |
|---|---|
| Antimony trisulphide . . . . . | $Sb_2S_3$. |
| Antimony pentasulphide . . . | $Sb_2S_5$. |

**ıntimony Trisulphide,** $Sb_2S_3$.—This compound occurs native the mineral *stibnite*, or *grey antimony ore.* It is prepared by .ting a mixture of powdered antimony and sulphur (in propor- ı required by the formula) beneath a layer of fused sodium oride in a crucible. It is also formed when sulphuretted hydro- ı is passed through a solution of antimony trichloride, or a ıtion of tartar emetic—

$$2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl.$$

**'roperties.**—Antimony trisulphide as it occurs native, and as ained by the direct union of antimony and sulphur, is a grey- ck crystalline substance; as prepared by precipitation with phuretted hydrogen, and subsequently drying at 200°, it is a :k-red amorphous powder, which when melted and slowly led, solidifies in the crystalline form. Antimony sulphide sub- es unchanged when heated in an inert gas, but when heated in sulphur dioxide is evolved, and antimonious oxide and tetroxide formed. Heated with hydrochloric acid, it evolves sulphuretted lrogen, and forms antimony trichloride—

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

**ıntimony Pentasulphide,** $Sb_2S_5$, is obtained when antimony ıtachloride is mixed with water, and sulphuretted hydrogen ,sed through the liquid—

$$2SbCl_5 + 5H_2S = Sb_2S_5 + 10HCl,$$

$$2SbO_2Cl + 5H_2S = Sb_2S_5 + 4H_2O + 2HCl.$$

---

n, and the term *metantimonates* was given to the salts belonging to the :r class. It is better, however, to adopt the same system of nomenclature the antimony compounds, as that which is in use for the similarly constituted :nic and phosphorus compounds—

| | Phosphates. | Arsenates. | Antimonates. |
|---|---|---|---|
| Ortho . . . | $M_3PO_4$ | $M_3AsO_4$ | ... |
| Pyro . . . | $M_4P_2O_7$ | $M_4As_2O_7$ | $M_4Sb_2O_7$ |
| Meta . . . | $MPO_3$ | $MAsO_3$ | $MSbO_3$ |

**Properties.**—Antimony pentasulphide is a dark, orange-red powder, which on being heated, is decomposed into the trisulphide and free sulphur.

Both of these antimony sulphides may be regarded as thio-anhydrides, for although no thio-acids derived from them are known, salts have been produced which may be viewed as derivatives of hypothetical thio-acids. When the trisulphide is either fused with caustic potash, or boiled in an aqueous solution, potassium thio-antimonite is formed—

$$2Sb_2S_3 + 4KHO = 3KSbS_2 + KSbO_2 + 2H_2O.$$

Similarly, when antimony pentasulphide is dissolved in potassium hydroxide, a mixture of antimonate and thio-antimonate is obtained—

$$4Sb_2S_5 + 24KHO = 5K_3SbS_4 + 3K_3SbO_4 + 12H_2O.$$

The following are illustrations of the thio-salts of antimony—

| Sulphide. | Hypothetical Acids. | Salts. |
|---|---|---|
| $Sb_2S_3$ . | (Ortho) $H_3SbS_3$. | Potassium thio-antimonite. $K_3SbS_3$. |
| | (Meta) $HSbS_2$. | Silver thio-antimonite, $AgSbS_2$. |
| | (Pyro) $H_4Sb_2S_5$. | Lead thio-antimonite, $Pb_2Sb_2S_5$. |
| $Sb_2S_5$ . . | (Ortho) $H_3SbS_4$. | Potassium thio-antimonate, $K_3SbS_4$. |
| | | Sodium thio-antimonate (Schlippe's salt) $Na_3SbS_4$. |
| | | Barium thio-antimonate, $Ba_3(SbS_4)_2$. |

Only ortho-thio-antimon*ates* are known.

## BISMUTH.

Symbol, Bi. Atomic weight = 207.5.

**Occurrence.**—Bismuth occurs most commonly in the uncombined condition. It is met with in combination with oxygen, as $Bi_2O_3$, in *bismuth ochre;* and in combination with sulphur, as $Bi_2S_3$, in *bismuth glance.*

**Mode of Formation.**—Bismuth is principally obtained from the native metal, and from ores with which metallic bismuth is associated. The broken-up ore is liquated by being heated in inclined iron pipes, when the bismuth readily melts and drains away.

Pure bismuth can be prepared from the crude metal thus obtained, by first dissolving it in nitric acid, forming bismuth nitrate,

$Bi(NO_3)_3$, and then precipitating the basic nitrate by the addition of water—

$$Bi(NO_3)_3 + 2H_2O = (BiO)NO_3,H_2O + 2HNO_3.$$

The basic nitrate is next dried, and heated in a crucible with charcoal; the salt is first converted into the trioxide by the action of heat, and the oxide is reduced then by the carbon—

$$2(BiO)NO_3.H_2O = Bi_2O_3 + N_2O_4 + O + 2H_2O.$$
$$Bi_2O_3 + 3C = 3CO + Bi.$$

**Properties.**—Bismuth is a lustrous white metal with a faint reddish tinge. It melts at 268.3°. If the molten metal be allowed to cool until partially solidified, and the remaining liquid be then poured off, obtuse rhombohedral crystals, closely approaching to the cube, are obtained.

The specific gravity of bismuth is 9.823; it is extremely brittle, and a poor conductor of electricity. Bismuth is unacted upon by dry air at ordinary temperatures; moist air tarnishes its surface. Heated in air, or oxygen, it burns, forming the trioxide. It is only slightly attacked by hydrochloric acid, but is converted by hot sulphuric acid into a basic sulphate.

Bismuth readily forms alloys with other metals, and imparts to them the useful properties of ready fusibility and hardness. The alloys known by the general name of *fusible metal* contain bismuth; thus, *Wood's fusible metal*, which melts at 65°, consists of 4 parts of bismuth, 2 of lead, 1 of tin, and 1 of cadmium.

## *COMPOUNDS OF BISMUTH WITH THE HALOGENS.*

Compounds represented by the following formulæ are known—

| | | | |
|---|---|---|---|
| $BiF_3$ | $BiCl_3$ | $BiBr_3$ | $BiI_3$. |
| — | $(BiCl_2)_2$ | $(BiBr_2)_2$? | — |

**Bismuth Trichloride,** $BiCl_3$, may be prepared, by passing dry chlorine over powdered bismuth gently heated in a retort. A yellow liquid is first formed, after which the stream of chlorine is stopped and the liquid distilled, when the trichloride sublimes in the form of crystals. It may also be obtained by distilling a mixture of powdered bismuth and mercuric chloride—

$$Bi + 6HgCl_2 = 3Hg_2Cl_2 + 2BiCl_3.$$

**Properties.**—Bismuth trichloride is a white, extremely deliquescent, crystalline compound. Heated in an atmosphere of chlorine, it melts to a yellow liquid. It is decomposed by water with the precipitation of bismuth oxychloride—

$$BiCl_3 + H_2O = 2HCl + BiOCl.$$

**Bismuth Dichloride,** $(BiCl_2)_2$, is obtained by the prolonged heating of mercurous chloride and finely powdered bismuth to 230° in a sealed tube. The mixture melts, and mercury collects at the bottom, and on cooling, the dichloride solidifies as a black, extremely deliquescent solid upon the surface of the mercury. When heated above 300°, the dichloride is resolved into the trichloride and metallic bismuth. The molecular weight of the compound is unknown.

**Bismuth Tribromide,** $BiBr_3$, is prepared by gradually adding bromine to powdered bismuth, and slightly warming the mixture for some time. The bromide sublimes in the form of golden yellow, deliquescent crystals, which are decomposed by water, forming oxybromide, BiOBr.

**Bismuth Tri-iodide,** $BiI_3$, is prepared by subliming a mixture of iodine and bismuth. The sublimate is afterwards finely powdered and again sublimed, and the product finally distilled in a stream of carbon dioxide, when it forms dark grey crystals, with a bright metallic lustre. Boiling water decomposes the compound, with formation of bismuth oxyiodide, BiOI.

## *COMPOUNDS OF BISMUTH WITH OXYGEN.*

Four oxides of bismuth are known, namely—

| | | |
|---|---|---|
| Bismuth | dioxide (*Hypobismuthous oxide*) . . | $Bi_2O_2$. |
| „ | trioxide (*Bismuthous oxide*) . . | $Bi_2O_3$. |
| „ | tetroxide (*Hypobismuthic oxide*) . . | $Bi_2O_4$. |
| „ | pentoxide (*Bismuthic oxide*) . . | $Bi_2O_5$. |

None of these compounds is an acid-forming oxide, although, with the exception of the first, they all form hydrated oxides. These hydrated oxides have no acidic properties, and no salts have been obtained in which the acidic portion of the molecule consists of bismuth and oxygen. All the four oxides, when acted upon by acids, yield the same series of salts, in which the bismuth fulfils the functions of a trivalent element, replacing three atoms of hydrogen. In the case of the dioxide, metallic bismuth is deposited, thus—

$$3Bi_2O_2 + 6H_2SO_4 = 2Bi_2(SO_4)_3 + 2Bi + 6H_2O.$$

While with the higher oxides oxygen is evolved—

$$Bi_2O_5 + 6HNO_3 = 2Bi(NO_3)_3 + 2O + 3H_2O.$$

Bismuth trioxide is the most stable and the most important of the oxides; when heated in air, the remaining three compounds are converted into the trioxide; the dioxide by oxidation, and the tetroxide and pentoxide by loss of oxygen. The trioxide alone is unchanged on being heated in air or oxygen.

**Bismuth Dioxide**, $Bi_2O_2$.—This oxide is prepared by adding a mixed solution of bismuth trichloride and stannous chloride to an excess of a 10 per cent. solution of caustic potash, air being excluded: potassium stannate is formed, and bismuth dioxide is precipitated—

$$SnCl_2 + 2BiCl_3 + 10KHO = Bi_2O_2 + 8KCl + K_2SnO_3 + 5H_2O.$$

**Properties.**—The precipitated compound, after being washed in dilute caustic potash, and dried in vacuo, is obtained as a black crystalline powder. When heated in air it smoulders, uniting with oxygen to form the trioxide. When moist it oxidises spontaneously—

$$Bi_2O_2 + O = Bi_2O_3.$$

**Bismuth Trioxide**, $Bi_2O_3$, is formed when the metal is burnt in air or oxygen. It may also be obtained by heating the hydrated oxides, the carbonate, or basic nitrate, thus—

$$Bi_2O_3,H_2O = Bi_2O_3 + H_2O.$$
$$Bi_2O_3,CO_2 = Bi_2O_3 + CO_2.$$
$$2(BiO)NO_3,H_2O = Bi_2O_3 + N_2O_4 + O + 2H_2O.$$

**Properties.**—Bismuth trioxide is a cream-coloured powder, insoluble in and unacted upon by water, and is the only oxide of bismuth which is unchanged when heated in the air or in oxygen. It dissolves in acids, forming salts of bismuth—

$$Bi_2O_3 + 6HNO_3 = 3H_2O + 2Bi(NO_3)_3.$$
$$Bi_2O_3 + 3H_2SO_4 = 3H_2O + Bi_2(SO_4)_3.$$

With small quantities of hydrochloric acid it first forms bismuth oxychloride, BiOCl, which dissolves in additional acid, yielding the trichloride—

$$Bi_2O_3 + 2HCl = H_2O + 2BiOCl.$$
$$BiOCl + 2HCl = H_2O + BiCl_3.$$

None of these compounds is soluble in water without the presence of excess of the acid. Water alone converts them into insoluble basic salts, and free acid, which in the state of extreme dilution is unable to exert any solvent action. Thus, in the case of the nitrate, when water is added, this compound is decomposed into the basic nitrate and free nitric acid—

$$Bi(NO_3)_3 + 2H_2O = (BiO)NO_3,H_2O + 2HNO_3.$$

Bismuth trioxide forms three hydrates, represented by the formulæ—

$$Bi_2O_3,H_2O \qquad Bi_2O_3,2H_2O \qquad Bi_2O_3,3H_2O$$

These hydrates have no acid properties, and are incapable of combining with bases to form salts, but themselves play the part of a base, uniting with acids to form bismuth salts.

The trihydrate is obtained, by pouring an acid solution of bismuth nitrate into an excess of strong aqueous ammonia—

$$2Bi(NO_3)_3 + 6NH_3H_2O = 6NH_4(NO_3) + Bi_2O_3,3H_2O.$$

Heated to 100°, it is converted by loss of water into the monohydrate—

$$Bi_2O_3,3H_2O = Bi_2O_3,H_2O + 2H_2O.$$

**Bismuth Tetroxide,** $Bi_2O_4$, is formed by the action of potassium hypochlorite upon the trioxide, the product being dried at 180°—

$$Bi_2O_3 + KClO = Bi_2O_4 + KCl.$$

**Properties.**—Bismuth tetroxide is a brownish-yellow powder, which readily parts with an atom of oxygen, and passes into the trioxide.

**Bismuth Pentoxide,** $Bi_2O_5$, is prepared by passing chlorine into a nearly boiling solution of caustic potash, in which is suspended a quantity of bismuth trioxide—

$$Bi_2O_3 + 4KHO + 2Cl_2 = 4KCl + H_2O + Bi_2O_5,H_2O.$$

**Properties.**—Bismuth pentoxide is a red powder, which is readily deoxidised into the tetroxide and trioxide by heat. It combines with water, forming the hydrate $Bi_2O_5,H_2O$, but with excess of water it is gradually deoxidised into hydrates of the tetroxide or trioxide.

Bismuth pentoxide is reduced, with evolution of oxygen, by both nitric and sulphuric acids—

$$Bi_2O_5 + 3H_2SO_4 = Bi_2(SO_4)_3 + 3H_2O + O_2.$$

With hydrochloric acid it behaves in the usual manner of peroxides, causing the evolution of chlorine—

$$Bi_2O_5 + 10HCl = 2BiCl_3 + 5H_2O + Cl_2.$$

**Bismuth Trisulphide,** $Bi_2S_3$.—This compound is the only compound of bismuth with sulphur that is known with certainty. It occurs native as the mineral *bismuth glance.*

It is precipitated when sulphuretted hydrogen is passed into a solution of a bismuth salt—

$$2Bi(NO_3)_3 + 3H_2S = Bi_2S_3 + 6HNO_3.$$

It is also obtained by heating together the requisite proportions of bismuth and sulphur.

**Properties.**—As obtained by precipitation, bismuth sulphide is a dark brown, almost black powder; the native sulphide forms steel-grey lustrous crystals.

It is decomposed, when strongly heated, into its constituent elements. Bismuth sulphide differs from the corresponding antimony and arsenic compound, in not being dissolved by alkaline hydrates or sulphides.

# CHAPTER IV

## *THE ELEMENTS OF GROUP I. (FAMILY A.)*

THIS family comprises the following five elements, known as the *alkali metals*—

| | Atomic Weights. | Melting-points. |
|---|---|---|
| Lithium (Li) | 7.01 | 180° |
| Sodium (Na) | 22.99 | 95.6° |
| Potassium (K) | 39.03 | 62.5° |
| *Rubidium* (Rb) | 85.2 | 38.5° |
| *Caesium* (Cs) | 132.7 | 26.5° |

The most important, and the most abundant of these elements, are potassium and sodium, which also were the first to be discovered, having been isolated by Davy in the year 1807. The element lithium, although widely distributed in nature, is for the most part found only in minute quantities: the element was first isolated by Bunsen in the year 1855. The two remaining elements are still rarer substances, usually met with in very minute quantities accompanying sodium and potassium. Both of these elements were discovered by Bunsen by means of the spectroscope—caesium in 1860, and rubidium in the following year.

All these elements are soft, silvery-white metals, which may be readily cut with a knife, and which rapidly tarnish in the air. They all decompose water at the ordinary temperature. The members of this family exhibit that gradation in properties which is met with in all similar families. Thus, their melting-points gradually decrease as their atomic weights rise, as will be seen from the figures given above. Their chemical activity also steadily increases as we pass from lithium to caesium. Thus, in the case of their behaviour in contact with water; potassium, when thrown upon cold water, decomposes that liquid with sufficient energy to cause the ignition of the hydrogen which is evolved: sodium under the same conditions melts and floats about upon the surface, but the action is not sufficiently energetic to effect the inflammation of the gas, unless the water be previously heated; while with lithium, even with boiling water, the temperature produced by the reaction

:s not rise to the ignition-point of hydrogen. The same is also n in the spontaneous oxidation of these elements when they are ›osed to the air. Thus, lithium when cut with a knife, although s soon covered with a film of oxide, nevertheless retains its ght metallic surface for some seconds : sodium tarnishes so ch more quickly, that the film of oxide appears almost to follow knife. When potassium is cut, the bright surface can scarcely seen, so rapid is the oxidation, and if left exposed, a fragment of metal soon begins to melt by the heat of its own oxidation, and quently spontaneously ignites. With rubidium and caesium the dation is even more rapid, and a fragment of these metals freely ›osed to the air very rapidly takes fire spontaneously.

[he electro-positive character of these elements gradually in-ases from lithium to caesium, which is the most electro-positive all the known elements.

[he term *alkali*, applied to metals of this family, was originally :d (before any distinction was made between potash and soda) to iote the salt obtained by treating the ashes of plants with water. ter on, in order to distinguish between this substance and what :ame known as the *volatile alkali* (*i.e.*, ammonium carbonate), was termed the *fixed alkali*. The first distinction between tash and soda, was based upon the erroneous belief that the mer was entirely of vegetable origin, while the latter was only be found in the mineral kingdom : hence the names *vegetable* *:ali* and *mineral alkali* were used to denote these two sub-nces, both of which were regarded as elementary bodies until )7, when Davy showed that they contained the two metals, tassium and sodium.

[he resemblance between the different members of this family, d between their compounds, is very close ; so much so, that in the se of sodium, potassium, rubidium, and caesium, there are scarcely y ordinary chemical reactions by which they can be distinguished. iey are all readily identified, however, by means of the spectro-›pe. When a minute quantity of a lithium salt is introduced on a loop of platinum wire, into the non-luminous Bunsen flame, : latter is tinged a brilliant crimson red colour : a potassium salt iilarly treated, colours the flame a delicate lilac, while a sodium npound gives a brilliant daffodil-yellow colour. The colour parted to a flame by rubidium and caesium salts, is indistinguish-le by the eye from that given by potassium compounds ; and, ›reover, when any of these are mixed with a sodium salt, the intense yellow emitted by the latter, completely masks the colours given by the others. By means of the spectroscope, not only are the apparently similar colours given by potassium, rubidium, and caesium readily distinguished, but the presence of any or all of them is easily detected, even when admixed with sodium salts. Spectrum analysis is based upon the fact, that light of different colours has different degrees of refrangibility, and therefore when passed through a prism, the different coloured rays are bent out of their straight course at different angles. Ordinary white light is composed of rays of all degrees of refrangibility, *i.e.*, rays of all colours: hence, when a beam of such light is passed through a prism, the various coloured rays are separated, and become spread out in the order of their refrangibility, from the least refrangible red at the one extreme, to the deep violet at the other. This familiar "rainbow" coloured band of light is termed the *continuous spectrum*.

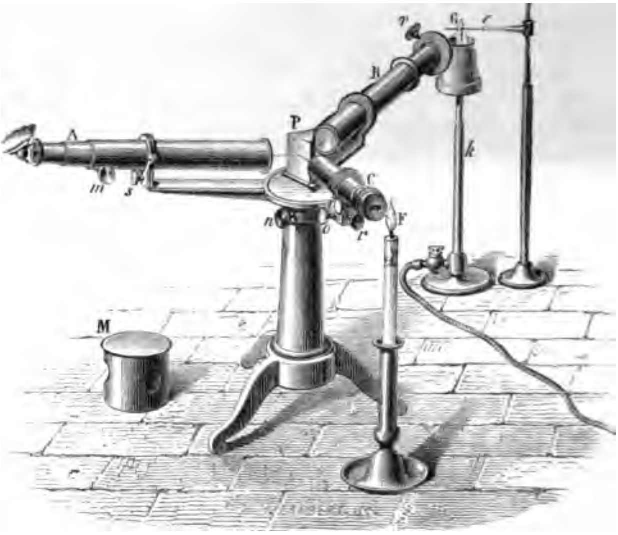

FIG. 124.

A simple form of spectroscope is seen in Fig. 124. The light is caused to pass through a narrow slit at the end of the fixed telescope B. If the prism P be removed, and the telescope A be moved round so as to be in a continuous line with B, a magnified image of the slit is seen by the observer. When the prism is replaced, and A is moved into such a position that the bent rays fall upon its lens, the continuous spectrum is seen, which is an infinite number of strips of light (corresponding to the image of the slit) of all colours, arranged side by side. If the light to be examined, instead of being ordinary white light, were composed of rays all of one degree of infrangibility (*i.e.*, monochromatic light), there would be produced only a single image of the slit, which would fall in that position corresponding to the particular degree of refrangibility of the light. Such a monochromatic light is produced when a sodium salt is heated in a Bunsen flame; if, therefore, a salt of this metal be introduced upon a loop of platinum wire into the non-luminous flame G, and the light, after passing through the prism, be observed through A, instead of a continuous spectrum, there will be seen a single image of the slit, falling in the brightest yellow part of the spectrum. When the sodium salt is replaced by a lithium salt, it is seen that two images of the slit are obtained, one in the red and the other in the yellow regions of the spectrum. The light emitted from this element consists of rays of two degrees of refrangibility. We say, therefore, that the spectrum of sodium is one yellow *line*,* and that of lithium consists of one red and one yellow *line*. In order to distinguish the positions of, for example, the yellow lithium line and that given by sodium, an image of a graduated scale, illuminated by the candle flame F, is also thrown into the telescope A.

If salts of sodium and lithium mixed together be introduced into the flame G, then three images of the slit are seen, namely, the yellow line given by the sodium, the yellow line of the lithium, situated slightly nearer the red, and the lithium red line.

Potassium, like lithium, gives a light of two degrees of refrangibility, forming consequently two images of the slit, one in the deep red and the other in the deep violet; if, therefore, lithium, sodium, and potassium salts are mixed, and examined by the spectroscope, five lines are seen (Fig. 125), namely, two red (one belonging to lithium and one to potassium), two yellow (one belonging to lithium and one to sodium), and the violet line of potassium.

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* In reality, when examined by a higher dispersive power, the sodium line is seen to be a group of lines.

When analysed in this manner, the lights emitted by rubidium and caesium compounds, are seen to be totally different from each other, and from potassium. The spectrum of rubidium consists of two prominent lines in the violet (nearer the blue region than that belonging to potassium), two brilliant red lines (very near the potassium red line), and a number of less brilliant lines in the orange, yellow, and green. That of caesium consists of two brilliant blue lines, two bright red lines (near the lithium red line), and a number of less prominent lines in the yellow and green. It will be seen, therefore, that the three elements potassium, rubidium, and caesium may be at once sharply distinguished by this optical method of analysis, although they so closely resemble one another in their chemical behaviour, as to render it highly probable that the separate existence of the two latter would never have been discovered by chemical methods alone.

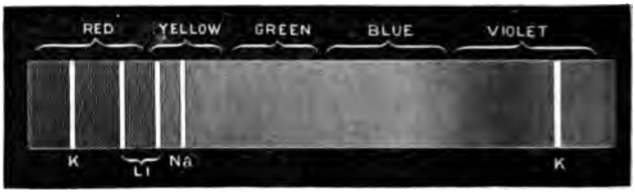

FIG. 125.

Indeed, before the discovery of caesium by Bunsen, a rare mineral known as *Pollux* (now known to contain caesium), was mistaken for a potassium mineral.*

The element lithium, the member of the family that belongs to the *Typical series*, exhibits certain characteristic differences from the other members. This is seen particularly in the case of the carbonate and phosphate of this element. Lithium carbonate is so little soluble in water, that it is precipitated by the addition of carbonate of either sodium or potassium to a solution of a lithium compound. The phosphates of all the other members are readily soluble in water, while lithium phosphate is almost insoluble, and is precipitated from solutions of a lithium salt by the phosphates of either sodium or potassium. In these two compounds, the carbonate and phosphate, lithium behaves more like one of the metals of the alkaline earths.

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* The student should consult special works on spectrum analysis.

All the metals of this family are monovalent, and replace each other, atom for atom, in chemical compounds.

## POTASSIUM.

Symbol K. Atomic weight = 39.03.

**Occurrence.**—In combination this element is widely distributed in nature. It forms an essential constituent of many of the common silicates, and rocks, which form the earth's crust. From these rocks, by processes of disintegration, the potassium compounds find their way into the soil, from whence they are absorbed by plants, which can only flourish in a soil that contains compounds of potassium. Most of the potassium found in plants is present in combination with organic acids.

From the vegetable kingdom, potash passes directly into the bodies of animals. The material known as *suint*, which is the oily perspiration of the sheep, that accumulates in, and is extracted from, the wool, consists of the potassium salt of an organic acid (sudoric acid). In the form of chloride and sulphate, potassium is present in sea water and many mineral springs. As nitrate it is found as a crystallised efflorescence upon the soil, notably in Peru and Chili, where it is associated with sodium nitrate. The largest supplies of potassium compounds are met with in the great saline deposits of Stassfurt, where the element is found as chloride (KCl) in *sylvine*, as a double chloride of potassium and magnesium ($KCl,MgCl_2,6H_2O$) in *carnallite*, and as a mixed sulphate in *kainite* ($K_2SO_4,MgSO_4,MgCl_2,6H_2O$).

**Modes of Formation.**—(1.) The method by which Davy first effected the isolation of potassium was by the electrolysis of potassium hydroxide: the method may be illustrated by the experiment represented in Fig. 126. A small quantity of potassium hydroxide is gently heated in a platinum capsule, which is connected to the positive terminal of a powerful battery. A stout platinum wire, flattened out at one end, is made the negative pole. When this is introduced into the fused potash, a brisk evolution of gas takes place, and minute beads of metallic potassium make their appearance in the liquid, and upon the negative electrode, some of which ignite upon the surface. The decomposition takes place according to the equation—

$$2KHO = H_2 + O_2 + K_2.$$

(2.) Potassium may also be obtained by allowing melted potassium hydroxide to pass over iron turnings heated to whiteness, when the magnetic oxide of iron is formed—

$$4KHO + 3Fe = Fe_3O_4 + 2H_2 + 2K_2.$$

This is known as Gay-Lussac and Thénard's method.

(3.) The method devised by Brunner, and modified by Wöhler, Deville, and others, consisted in heating to whiteness an intimate mixture of potassium carbonate and carbon. This mixture was obtained by first igniting in a covered iron pot, crude tartar (hydrogen potassium tartrate, or cream of tartar), which was thereby decomposed as indicated by the equation—

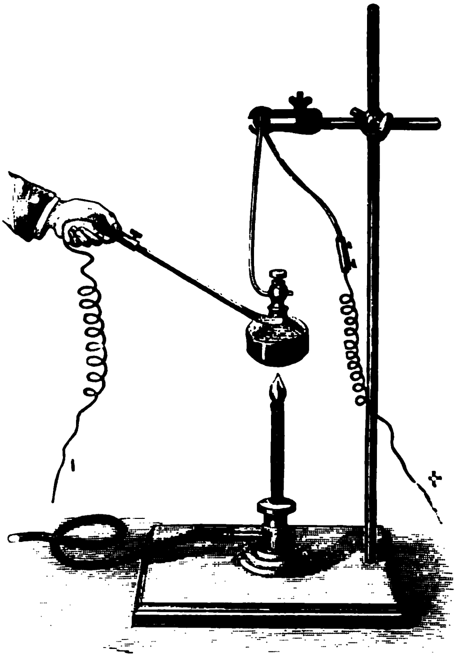

FIG. 126.

$$2HKC_4H_4O_6 = K_2CO_3 + 3C + 5H_2O + 4CO.$$

charred mass was then introduced into an iron retort (*P*, 27), and strongly heated in the furnace, when the potassium nate was reduced by the carbon as follows—

$$K_2CO_3 + 2C = 3CO + K_2.$$

soon as the potassium began to be formed, which was readily

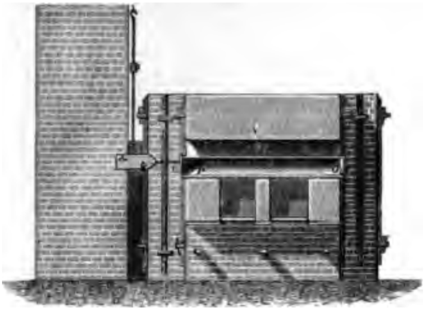

FIG. 127.

ained by the green appearance of the vapour, seen on looking the open mouth of the retort, the condenser was attached. onsisted of a flat, shallow iron tray, *b* (Fig. 128), upon which tted the cover *a*, the two portions being clamped together. bject of this special form of nser is to cool the potassium pidly as possible, for it is that unless the metal is ly cooled, it combines with arbon monoxide, forming a explosive compound (be- to have the composition $)_6$). By the use of this of condensing apparatus the tion of this compound is ed to a minimum, but not ly prevented.

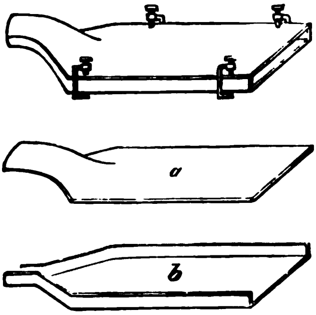

FIG. 128.

A more recent method by potassium (and sodium) pared on a manufacturing scale, was devised by Castner

(1886). In this process potassium hydroxide is strongly heated with a carbide of iron, having approximately the composition $CFe_2$. (This compound is obtained by heating a mixture of pitch and finely divided iron.)

The potassium hydroxide, with the powdered carbide of iron, is introduced into large egg-shaped retorts, one of which is represented in Fig. 129. These retorts are placed upon hydraulic lifts, so that they can be lowered away from their covers, to the ground-level, in order to be discharged at the end of the distillation. The retorts are heated by gaseous fuel, and the metal, as it distils, is passed into long narrow cast-iron condensers, from which it drops into iron pots, and is protected from oxidation by mineral oil. The reaction which takes place may be represented by the equation—

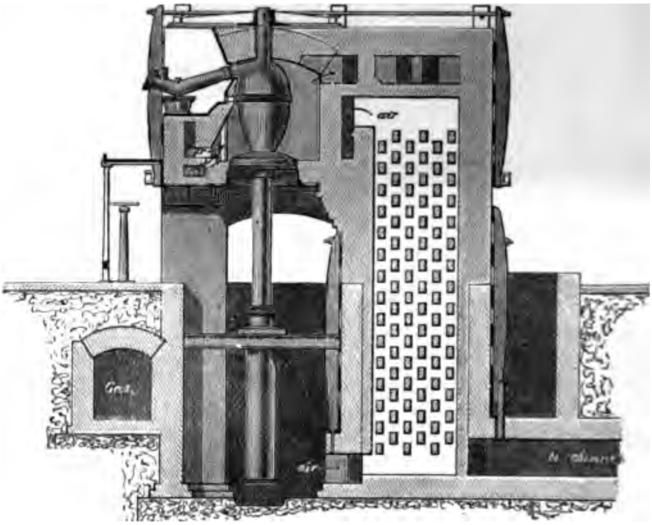

FIG. 129.

$$6KHO + 2C = 2K_2CO_3 + 3H_2 + K_2.$$

By avoiding any excess of carbon, no carbon monoxide is produced, and hence there is no formation of the explosive compound of this gas with potassium.

**Properties.**—Potassium is a lustrous, white metal, which at rdinary temperatures is sufficiently soft to be moulded between he fingers ; at 0° it is brittle, and shows a crystalline fracture. The metal is readily crystallised by melting a quantity of it in a acuous tube, and when it has partially solidified, pouring the still iquid portion to the other end of the tube. Potassium melts at 2.5°, and when boiled gives an emerald-green vapour. The metal is rapidly acted on by ordinary air, its freshly cut surface ecoming instantly covered with a film of oxide, which, by absorption of atmospheric moisture and carbon dioxide, passes first into he hydroxide and finally into the carbonate. Potassium is therefore usually preserved beneath naphtha, or some other liquid devoid of oxygen.

When potassium is volatilised in a vacuous tube, the thin film of metal which condenses upon the cool portion of the tube, is seen to ossess a rich violet-blue colour, when viewed by transmitted light. The density of potassium vapour is about 40 (Dewar and Scott), howing that in the vaporous condition the molecules are montomic.

Potassium dissolves in liquefied ammonia, forming a deep indigo olution (p. 243). When potassium is thrown upon water, that quid is decomposed with sufficient energy to cause the ignition f the liberated hydrogen (p. 151). When heated in carbon ioxide, potassium takes fire, forming potassium carbonate, and arbon (p. 267). Heated in carbon monoxide, it forms the explosive ompound already mentioned. Potassium takes fire spontaneously n contact with the halogens, forming the haloid compounds of he metal. When heated in hydrogen, it absorbs the gas, forming brittle lustrous substance, which inflames spontaneously in the ir. This compound has the composition $K_4H_2$.

When heated in nitric oxide, potassium burns, forming a mixture f potassium nitrate and nitrite (Holt and Sims).

**Oxides of Potassium.**—When potassium is heated in ordinary ir, it takes fire and burns, giving rise to two oxides, viz., potassium onoxide, $K_2O$, and peroxide, $K_2O_4$. *Perfectly dry* air or oxygen s without action upon potassium.

**Potassium Peroxide**, $K_2O_4$, may be obtained by melting potasum in an atmosphere of nitrogen, and gradually displacing the itrogen by moderately dry oxygen. It is also produced by heating otassium in nitrous oxide.

Potassium peroxide is a yellow powder, which, when strongly heated, is converted into the monoxide $K_2O$ and oxygen. When thrown into water, oxygen is evolved, potassium hydroxide and hydrogen peroxide being formed—

$$K_2O_4 + 2H_2O = 2KHO + H_2O_2 + O_2.$$

By the regulated combustion of potassium in nitrous oxide, Holt and Sims have obtained compounds having the composition $K_2O_2$ and $K_2O_3$. The latter, in contact with the air, undergoes active oxidation into $K_2O_4$.

**Potassium Hydroxide** (*caustic potash*), KHO, is prepared by adding lime to a dilute boiling solution of potassium carbonate, in iron vessels, when calcium carbonate is precipitated and potassium hydroxide remains in solution—

$$K_2CO_3 + Ca(HO)_2 = CaCO_3 + 2KHO,$$

the reaction being complete, when the addition of an acid to a small test sample of the clear liquor, produces no effervescence. This reaction is a reversible one, and if the concentration is beyond a certain limit, the potassium hydroxide reacts upon the calcium carbonate, reforming potassium carbonate. The liquid is therefore constantly maintained at a certain state of dilution during the reaction, at the completion of which the mixture is allowed to settle, and the clear solution is then partially concentrated in iron vessels, and finally in silver, until on cooling, the substance solidifies. It is then usually cast into sticks.

Caustic potash is a white brittle solid; it is extremely deliquescent, and dissolves in water with evolution of heat, forming a highly caustic liquid. The solid, as well as the solution, readily absorbs carbon dioxide, and is employed in the laboratory for this purpose when it is desired to deprive a gas of the last traces of any admixed carbon dioxide. A hot saturated solution of potassium hydroxide, when cooled, deposits crystals of a hydrate having the composition $KHO,2H_2O$.

**Potassium Fluoride**, KF.—This salt is prepared by neutralising aqueous hydrofluoric acid with potassium carbonate, and evaporating the solution in a platinum vessel, when the salt is obtained in the form of deliquescent cubical crystals. Potassium fluoride dissolves in aqueous hydrofluoric acid with evolution of heat, forming the acid fluoride of potassium, HF,KF, which is obtained as an anhydrous salt when the solution is evaporated to dryness and heated to 110°. This salt is not deliquescent. When heated to a

:ed heat it decomposes into the normal salt and hydrofluoric (see p. 312).

**tassium Chloride,** KCl.—This salt is found in sea water, and ıt one time obtained as a secondary product in the manufacture omine from sea salt, and of iodine from seaweed, as well as in us other industrial processes. At the present day it is almost ısively obtained from the enormous deposits of carnallite at ;furt. The method by which potassium chloride is obtained this double salt, $KCl,MgCl_2,6H_2O$, is based upon the fact, when dissolved in water, the salt dissociates into its two :ituents; and when the solution is concentrated, the more uble potassium chloride first separates out, leaving the magım chloride in solution.

practice, the crushed crude carnallite is treated with boiling ıer liquors from previous operations, in large tanks into which n can be driven. These mother liquors are practically a ıg solution of magnesium chloride, and it is found that while ssium chloride is readily soluble in this liquid, the sodium ·ide and magnesium sulphate which are present in the crude allite are only slightly dissolved by it, and are therefore left ıd in the residue.

ıe muddy liquid is allowed to settle for about an hour, when it awn off into large iron crystallising tanks. The salt which is deposited, contains from 80 to 90 per cent. of potassium ·ide, the remainder being mainly sodium and magnesium ·ides.

ıe mother liquor from these crystallising tanks, is either used ı for treating a fresh charge of mineral, or is further evaporated, ı crystals of *carnallite* separate out; for it is found that when ımount of magnesium chloride present, is greater than three s the proportion of potassium chloride in the solution, the liquid ·ystallising, deposits the double chloride of the two metals. The ıre potassium chloride from the crystallising tanks is purified by ıing with cold water, in which the salt is only slightly soluble, by subsequent recrystallisation. Potassium chloride crystal- like the chlorides of sodium, rubidium, and caesium, in cubes.

**ıtassium Chlorate,** $KClO_3$.—When chlorine is passed into a ion of potassium hydroxide, a mixture of potassium chlorate chloride is obtained, thus—

$$6KHO + 3Cl_2 = KClO_3 + 5KCl + 3H_2O.$$

The two salts in solution may be separated by crystallisat the chlorate being much less soluble in cold water than chloride.

On the manufacturing scale, potassium chlorate is obtaine passing chlorine into milk of lime, when a mixture of cal chlorate and chloride is formed—

$$6Ca(HO)_2 + 6Cl_2 = Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O.$$

The operation is conducted in cast-iron cylinders conne in series, one of which is shown in section in Fig. 130, furni

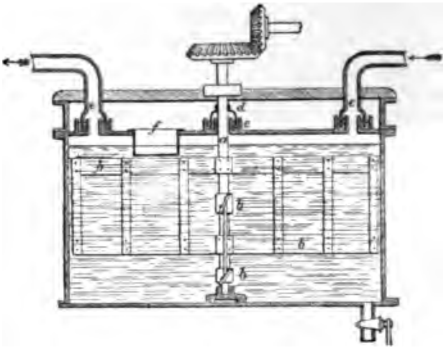

FIG. 130.

with mechanical stirring gear, *a*, *b*, *b*. The shaft, and the conveying the chlorine into, and from the vessel, are connect it by means of the water-sealed joints *c*, *e*, *e*. The manhole short wide leaden pipe, dipping a few inches into the liquid, allows of the periodic withdrawal of samples for examina Several reactions are involved in the final formation of the cal chlorate; in the first case calcium hypochlorite is prod thus—

$$2Ca(HO)_2 + 2Cl_2 = Ca(OCl)_2 + CaCl_2 + 2H_2O.$$

The calcium hypochlorite then passes into a mixture of chl and chloride in accordance with the equation—

$$3Ca(OCl)_2 = Ca(ClO_3)_2 + 2CaCl_2.$$

The second change is brought about by the operation of amely, rise of temperature, and the presence of excess of Heat *alone* is incapable of converting more than a ɔportion of the hypochlorite into chlorate, for the former d is at the same time decomposed into calcium chloride oxygen. The excess of chlorine is believed to act, through vention of hypochlorous acid, HOCl, merely as a carrier n, reducing two molecules of calcium hypochlorite to and oxidising the third to chlorate, thus—

$$Cl)_2 + 2Cl_2 + 2H_2O = CaCl_2 + 4HOCl + 2Ca(OCl)_2 =$$
$$2CaCl_2 + Ca(ClO_3)_2 + 2Cl_2 + 2H_2O.$$

ɔsorption of chlorine by the milk of lime is attended with of heat; care is taken to prevent the temperature from ove about 70°, otherwise loss results by the decomposition hlorite with evolution of oxygen, thus—

$$Ca(OCl)_2 = CaCl_2 + O_2.$$

the formation of calcium chlorate is complete, the liquid d to settle, and is then run into concentrating pans, where site amount of potassium chloride in solution demanded llowing equation, is added—

$$Ca(ClO_3)_2 + 2KCl = CaCl_2 + 2KClO_3.$$

quid is then concentrated in iron pans and allowed to e, when the moderately soluble potassium chlorate sepa-, leaving the very soluble calcium chloride in solution. rate is afterwards purified by recrystallisation.

m chlorate, although only moderately soluble in water, is much ıle in a strong solution of calcium chloride, hence there is always a y about 10 per cent.) of chlorate in this process. Péchmey's pro-viating this, consists in concentrating the liquid, obtained by the n of the lime, to a definite specific gravity, and then cooling it to about 78 per cent. of the calcium chloride crystallises out. The ıor, containing all the calcium chlorate, and only the comparatively ortion of calcium chloride, is then treated with potassium chloride

ium chlorate crystallises in white tables, belonging to the ımetric system, which when of large size often exhibit fine iridescent colours. 100 parts of water at 0° dissolve 3.3 parts of the salt; while at 100°, 59 parts are dissolved.

Potassium chlorate is used largely in the manufacture of matches, on account of the ease with which it gives up its oxygen: thus, if a small quantity of the finely powdered salt be carefully mixed with an equally small amount of red phosphorus, the friction caused by lightly rubbing it with a spatula, is sufficient to cause the mixture to detonate violently. Similarly, when powdered potassium chlorate and sulphur are rubbed together in a mortar, the mixture explodes with violence. Potassium chlorate is also largely employed in pyrotechny, especially in the production of coloured effects, where a fiercely burning mixture is required.

Potassium chlorate melts between 360° and 370°, and at a temperature about 380° begins to evolve oxygen.

**Potassium Perchlorate,** $KClO_4$.—When the chlorate is heated, it first melts and begins to give off oxygen; but it soon begins to partially solidify, owing to the formation of potassium perchlorate, and the evolution of oxygen stops unless a stronger heat be applied. The reaction at this stage is expressed by the equation—

$$2KClO_3 = KClO_4 + KCl + O_2.$$

The perchlorate is separated, by first treating the residue with cold water, which dissolves the greater part of the chloride, and afterwards with warm hydrochloric acid, which decomposes any remaining chlorate. The salt is then purified by crystallisation.

Potassium perchlorate is very slightly soluble in cold water, 100 parts of water at 0° dissolving only 0.7 parts of the salt; while at 100°, 20 parts are dissolved.

**Potassium Bromide,** KBr, and **Iodide,** KI.—These two salts are obtained by similar methods. When bromine or iodine is added to a solution of potassium hydroxide, the reaction which takes place is exactly analogous to that in the case of chlorine (see Potassium Chlorate, above)—

$$6KHO + 3Br_2 = KBrO_3 + 5KBr + 3H_2O.$$

If the solution so obtained be evaporated by dryness, and the dry residue ignited, the bromate (or iodate) is decomposed, just as potassium chlorate is decomposed by heat, giving off its oxygen, and being converted into bromide (or iodide)—

$$KBrO_3 = KBr + 3O.$$

The residue, on being dissolved in water and recrystallised, yields pure potassium bromide (or iodide).

These salts are manufactured by decomposing ferrous bromide, $Fe_3Br_8$ (or iodide, $Fe_3I_8$), with potassium carbonate, thus—

$$Fe_3Br_8 + 4K_2CO_3 = Fe_3O_4 + 8KBr + 4CO_2.$$

The ferrous bromide is obtained by adding bromine to moistened iron borings (see Manufacture of Bromine).

Potassium iodide and bromide both crystallise in cubes, and are both readily soluble in water. These salts are chiefly used for medicinal and photographic purposes.

**Potassium Sulphate,** $K_2SO_4$.—This salt is present in the Stassfurt deposits principally as *kainite*, $K_2SO_4,MgSO_4,MgCl_2,6H_2O$, and as *polyhalite*, $K_2SO_4,MgSO_4,2CaSO_4,2H_2O$. When kainite is treated with small quantities of water, or mother liquors from other processes, the extremely soluble magnesium chloride is removed, leaving the potassium magnesium sulphate; and on adding to this the requisite amount of potassium chloride, the following change takes place—

$$K_2SO_4,MgSO_4 + 3KCl = 2K_2SO_4 + KCl,MgCl_2.$$

From this solution the potassium sulphate crystallises out.

Potassium sulphate is also obtained by the action of sulphuric acid upon the chloride, by a process corresponding exactly to the first stage in the Leblanc soda process (*q.v.*)—

$$2KCl + H_2SO_4 = K_2SO_4 + 2HCl.$$

Potassium sulphate forms colourless rhombic crystals, containing no water of crystallisation, therein differing from sodium sulphate, which crystallises with ten molecules of water.

Potassium sulphate is largely used for agricultural purposes.

**Potassium Carbonate,** $K_2CO_3$.—This salt was formerly obtained exclusively from the ashes of wood and other land plants, and was known under the name of *pot-ashes*. The process is still carried on in parts of Canada and the United States. The wood is burned in pits, and the ashes are collected and lixiviated with water (with the addition of a small quantity of lime) in wooden tubs with perforated false bottoms. The liquid which is drawn off is evaporated to dryness, and usually calcined to burn away the organic matter. This material, known as American pot-ashes, contains varying quantities of caustic potash, on account of the previously added lime. The so-called American *pearl-ash* is a purer product, obtained by concentrating the liquor from the lixiviating tubs until the less soluble impurities crystallise out, and finally evaporating the mother liquor, containing the potassium carbonate, to dryness, and calcining the residue.

Potassium carbonate is also obtained from beet-root molasses, an uncrystallisable residue obtained in the manufacture of beet sugar, carried on chiefly in France. The syrup is fermented with yeast, whereby the sugar it contains is converted into alcohol, and then distilled. The residual liquid, known as *vinasse*, is evaporated to dryness; and from the black residue, termed "vinasse cinder," the potassium carbonate is extracted.

Potassium carbonate is obtained also from *suint*, which, as already stated, contains considerable quantities of potassium in the form of potassium sudorate. The sheep's wool is lixiviated with water, and the solution evaporated to dryness. The residue is heated in iron retorts, whereby the organic potassium salts are converted into carbonate, while at the same time ammonia, and an illuminating gas, are evolved. The carbonaceous residue is extracted with water, and the potassium carbonate separated by crystallisation.

Since the development of the Stassfurt potash supplies, these sources of potassium carbonate are rapidly sinking into the background, and the bulk of this compound is now manufactured from potassium sulphate by a process exactly similar to the Leblanc soda process (*q.v.*).

Potassium carbonate is not manufactured by a method analogous to the ammonia-soda process (Solvay), on account of the too great solubility of potassium bicarbonate (hydrogen potassium carbonate).

Pure potassium carbonate may be obtained by igniting cream of tartar (see page 472), and extracting with water; or by heating hydrogen potassium carbonate, which gives up water and carbon dioxide, thus—

$$2HKCO_3 = K_2CO_3 + H_2O + CO_2.$$

Potassium carbonate forms long prismatic crystals belonging to the monosymmetric system, and containing three molecules of water, $K_2CO_3,3H_2O$. The anhydrous salt is highly deliquescent, and very soluble in water.

**Hydrogen Potassium Carbonate** (*bicarbonate of potash*),

$HKCO_3$, is produced by passing carbon dioxide into an aqueous solution of the normal carbonate, thus—

$$K_2CO_3 + CO_2 + H_2O = 2HKCO_3.$$

This salt is much less soluble in water than the normal salt, and is readily purified by crystallisation.

**Potassium Nitrate** (*nitre, saltpetre*), $KNO_3$.—This salt has been known since very early times. It occurs as an efflorescence upon the earth, as a result of the oxidation of organic nitrogenous matter in the presence of the potash in the soil, and is found in the neighbourhood of villages, more especially in hot climates, where urine and other readily decomposable organic matters rich in nitrogen find their way into the surface soil. It has been shown that the process of nitrification which results in the formation of nitre under these circumstances, is due to the action of specific organisms, or microbes, and never takes place in their absence. At various times this natural process has been artificially carried on, by mixing manure and other decomposing refuse, with porous soil, lime, and wood ashes, and exposing the mixture in heaps which were moistened from time to time with drainage from manure. The *saltpetre earth*, collected from the natural sources, or from the artificial *nitre plantations*, on lixiviation with water, and subsequent evaporation, yielded crystals of potassium nitrate.

At the present time, potassium nitrate is almost exclusively obtained from sodium nitrate (*Chili saltpetre*), by treatment with potassium chloride derived from the Stassfurt supplies. The requisite quantities of the two solutions are run into a tank, and heated by means of steam, when the following double decomposition takes place—

$$NaNO_3 + KCl = NaCl + KNO_3.$$

The greater part of the sodium chloride is at once precipitated, and is removed by canvas filters. The clear liquid is then allowed to crystallise in tanks furnished with stirring gear, in order to cause the formation of small crystals, and the *nitre-meal* so obtained is purified by recrystallisation.

Potassium nitrate crystallises usually in rhombic prisms, but it can also be obtained in the form of small rhombohedral crystals, isomorphous with sodium nitrate.

The solubility of potassium nitrate rapidly increases with rise of temperature (see Solubility Curve, p. 131). 100 parts of water at 0° dissolve 13.3 parts; at 50°, 86 parts; and at 100°, 247 parts.

Nitre melts at 339°, and at a higher temperature loses oxygen and is converted into potassium nitrite: on this account it readily oxidises many of the elements when heated in contact with them. Thus, a fragment of charcoal or sulphur thrown upon melted nitre, takes fire and burns with great energy; in the one case with formation of potassium carbonate and carbon dioxide, and in the other of potassium sulphate and sulphur dioxide—

$$4KNO_3 + 5C = 2K_2CO_3 + 3CO_2 + 2N_2.$$
$$2KNO_3 + 2S = K_2SO_4 + SO_2 + N_2.$$

Nitre is chiefly used in the manufacture of gunpowder and in pyrotechny.

Gunpowder is a mixture of nitre, charcoal, and sulphur. The proportions in which these ingredients are present varies, within small limits, according to the special kind of powder, as will be seen from the following table (Abel and Nobel), giving analyses of various powders manufactured at Waltham Abbey.

| | Fine-grain. | Rifle Fine-grain. | Rifle Large-grain. | Pebble Powder. |
|---|---|---|---|---|
| Potassium nitrate | 73.55 | 75.04 | 74.95 | 74.67 |
| ,, sulphate | 0.36 | 0.14 | 0.15 | 0.09 |
| Sulphur | 10.02 | 9.93 | 10.27 | 10.07 |
| Charcoal | 14.59 | 14.09 | 13.52 | 14.22 |
| Water | 1.48 | 0.80 | 1.11 | 0.95 |

These proportions are very close to those which would be demanded by the equation—

$$2KNO_3 + S + 3C = K_2S + 3CO_2 + N_2,$$

which was at one time supposed to represent the change which takes place when gunpowder is exploded. In reality the decomposition is much more complex, and it has been shown that the solid products consist of mixtures of the following substances in varying proportions, depending upon the particular powder, and the conditions of firing—

Potassium carbonate.
,, sulphate.
,, sulphide.
,, thiosulphate.
,, thiocyanate.

Potassium nitrate.
,, oxide.
Ammonium sesquicarbonate.
Carbon.
Sulphur.

While the gases that are evolved consist of—

Carbon dioxide.
Nitrogen.
Carbon monoxide.
Sulphuretted hydrogen.
Marsh gas.
Oxygen.
Hydrogen.

From the combustion of one gramme of powder, the total weight of solids ranges from 0.55 to 0.58 gramme, and the total weight of the gaseous products from 0.45 to 0.42 gramme.

## *COMPOUNDS OF POTASSIUM WITH SULPHUR.*

Four sulphides of potassium have been obtained, namely—

| | |
|---|---|
| Potassium monosulphide . | $K_2S$, corresponding to the monoxide, $K_2O$. |
| Potassium trisulphide . | $K_2S_3$. |
| Potassium tetrasulphide . | $K_2S_4$, corresponding to the tetroxide, $K_2O_4$. |
| Potassium pentasulphide . | $K_2S_5$. |

Just as potassium decomposes water with evolution of hydrogen and formation of potassium hydroxide, so also, when heated in sulphuretted hydrogen (the sulphur analogue of water) it forms potassium hydrosulphide (the analogue of potassium hydroxide) and liberates hydrogen, thus—

$$H_2S + K = KHS + H,$$

when potassium hydroxide and hydrosulphide are mixed in equimolecular proportions, potassium monosulphide and water are formed—

$$KHO + KHS = K_2S + H_2O.$$

The liquid, on evaporation in vacuo, deposits reddish prismatic deliquescent crystals having the composition $K_2S,5H_2O$.

When potassium carbonate and sulphur are heated together, a mixture of the higher sulphides of potassium with potassium thiosulphate is obtained, thus—

$$3K_2CO_3 + \ 8S = 2K_2S_3 + K_2S_2O_3 + 3CO_2.$$
$$3K_2CO_3 + 12S = 2K_2S_5 + K_2S_2O_3 + 3CO_2.$$

The reddish-brown solid product was named by the early chemists ***hepar sulphuris***, or "liver of sulphur."

## SODIUM.

Formula, Na = 22.99.

**Occurrence.**—The most abundant natural compound of sodium is the chloride, which is present in sea-water, and in many salt lakes and springs. Enormous deposits of sodium chloride, or *rock-salt*, are found in Cheshire, Lancashire, and other parts of the world. As nitrate, this element occurs in large quantities in Chili and Peru; and in combination with silicic acid it is a constituent of many rocks.

**Modes of Formation.**—Sodium was first isolated by Davy, by the electrolysis of sodium hydroxide. It is now manufactured by processes exactly similar to those described for the preparation of potassium. Sodium, however, forms no explosive compound with carbon monoxide: hence in its manufacture, an excess of carbon in the ferrous carbide, is not detrimental.

**Properties.**—Sodium closely resembles potassium in its general properties. It is a soft, white metal which can be readily moulded by the fingers, and is easily pressed into wire. At − 20° it is hard. The colour of sodium vapour is violet, while the colour exhibited by a thin film of the metal, obtained by sublimation in vacuo, is greenish-blue. The vapour density of sodium is about 25 (Dewar and Scott), showing that this metal in the vaporous state is monatomic.

Like potassium, sodium dissolves in liquid ammonia, yielding a blue solution. When heated in the air, sodium burns, forming the monoxide, $Na_2O$, and peroxide, $Na_2O_2$. Perfectly dry air or oxygen is without action upon the metal.

When heated in hydrogen, sodium forms the hydride, $Na_4H_2$, analogous to the potassium compound, but not spontaneously inflammable in air. When this is heated to about 300° in vacuo, the whole of the hydrogen is evolved.

**Alloy of Sodium and Potassium.**—When these two metals are melted together beneath petroleum, an alloy is obtained which is liquid at ordinary temperatures. When prepared and preserved out of contact with air, the alloy resembles mercury in appearance. This alloy is employed in the construction of thermometers for registering high temperatures, where mercury would be inadmissible.

**Oxides of Sodium.**—Two oxides are known, viz., sodium monoxide, $Na_2O$, and sodium dioxide, or peroxide, $Na_2O_2$; both of which are formed when sodium burns in the air.

**Sodium Monoxide**, $Na_2O$, is obtained by burning sodium in a limited supply of moderately dry oxygen mixed with nitrogen, or in nitrous oxide, at a temperature not higher than 180°. It is also produced by heating sodium hydroxide with sodium—

$$NaHO + Na = Na_2O + H.$$

Sodium monoxide is an amorphous greyish-white solid, which combines with water, forming the hydroxide.

**Sodium Peroxide**, $Na_2O_2$, is obtained by allowing sodium to burn briskly in oxygen. It is a yellowish-white solid, which decomposes in contact with water, with considerable rise of temperature and evolution of oxygen—

$$Na_2O_2 + H_2O = 2NaHO + O.$$

The oxygen which is evolved contains appreciable quantities of ozone. When sodium peroxide is slowly added to water, or to dilute hydrochloric acid in the cold, hydrogen peroxide is formed—

$$Na_2O_2 + 2H_2O = 2NaHO + H_2O_2.$$

Sodium peroxide forms a crystalline hydrate of the composition, $Na_2O_2,8H_2O_2$ (p. 204). When heated in either nitrous or nitric oxides, it yields sodium nitrite; in the former case, with the elimination of nitrogen—

$$Na_2O_2 + 2N_2O = 2NaNO_2 + N_2.$$
$$Na_2O_2 + 2NO = 2NaNO_2.$$

**Sodium Hydroxide** (*caustic soda*), NaHO.—This compound is produced when sodium is brought into contact with water, and also when either sodium monoxide, or peroxide, is dissolved in water. On the large scale, caustic soda is prepared by the action of lime upon a boiling solution of sodium carbonate (see Caustic Potash)—

$$Na_2CO_3 + Ca(HO)_2 = CaCO_3 + 2NaHO.$$

The so-called *tank liquors* (obtained in the manufacture of sodium carbonate by the Leblanc process, *q.v.*) are heated to the boiling-point, and an excess of lime is stirred into the mixture. The sodium sulphide present in the tank liquor, is oxidised into sulphate by the combined action of air injected into the mixture, and of sodium nitrate, which is added for this purpose. The liquor, after being causticised, is decanted, or filtered, from the precipitated calcium carbonate, and is concentrated in large cast-iron hemispherical pans. The decomposition suffered by the sodium nitrate depends upon the temperature and concentration of the liquid: at 300° to 360° the change may be expressed by the equation—

$$NaNO_3 + 2H_2O = NaHO + NH_3 + 4O.$$

The liberated oxygen oxidises the sulphides to sulphates.

Sodium hydroxide is a white, strongly caustic, and highly deliquescent solid, closely resembling potassium hydroxide in its properties. It is soluble in water, with considerable rise of temperature, and a concentrated aqueous solution when cooled to − 8°, deposits a crystalline hydrate, having the composition $2NaHO,7H_2O$.

**Sodium Chloride,** NaCl.—Of the compounds of sodium with the halogens, the chloride is the most important. In warm climates, as upon the shores of the Mediterranean, sodium chloride is obtained by the evaporation of sea water in large shallow basins, or pools, constructed upon the sea-shore, and exposed to the sun's heat. As the brine concentrates in these *salterns*, the crystals of salt are raked off the liquid, and allowed to drain in heaps at the side of the pools. The mother liquors, known as *bitterns*, were formerly utilised for the extraction of the bromine which they contain.

Salt is obtained from salt-beds, where it is found in enormous deposits, either by direct mining operations, when the salt is sufficiently pure, or by first dissolving the material in water, whereby insoluble admixed impurities are removed, and afterwards evaporating the brine so obtained. The latter method is carried out by sinking borings through the upper strata of rock, and sending water down to the salt-beds beneath. The brine is then pumped up, and the salt obtained by evaporation. The first stage of the concentrating process, especially where the brine is not very strong, is in some parts carried on by exposing the liquid to the wind. This is effected by causing the solution to trickle over erections of brushwood known as *graduators* (Fig. 131), which are built so that the prevailing winds blow across them. The brine is pumped up into the wooden troughs running along the top, from which it escapes by a number of openings, *a*, *a*, *a*, and flows over the pile of brushwood down into the reservoir upon which the erection is constructed. In this way the solution is made to expose a large surface to the air, and it quickly reaches a concentration when it contains 20 per cent. of salt in the solution. The liquor is then evaporated in shallow iron pans by means of artificial heat, and as the salt crystallises it is lifted out by means of perforated iron skimmers. Salt obtained in this manner, always contains small quantities of other salts, such as sodium sulphate,

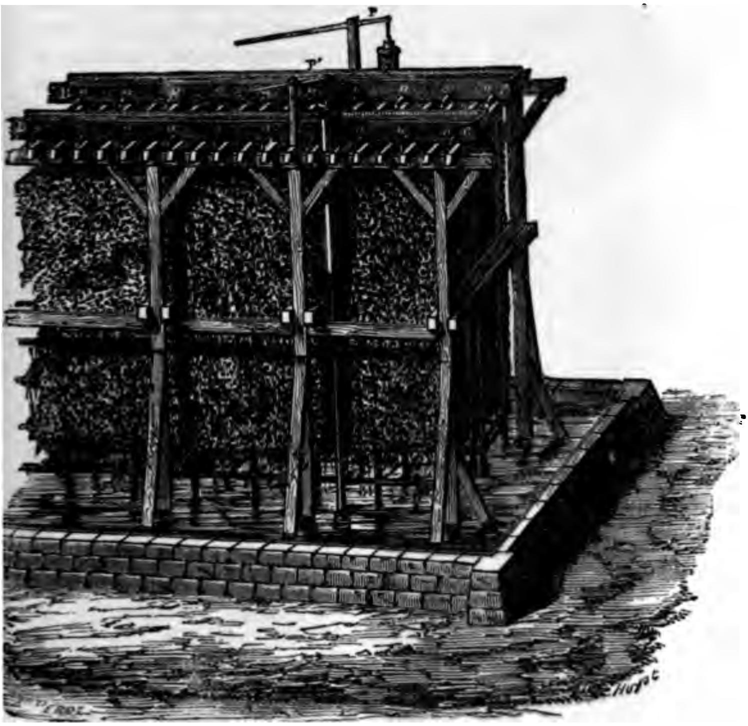

FIG. 131.

calcium sulphate, calcium and magnesium chlorides. The presence of chlorides of magnesium or calcium, causes the salt to become moist, especially in damp weather.

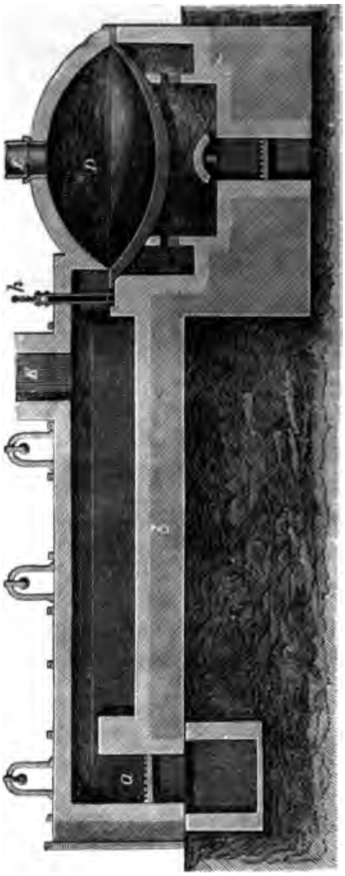

FIG. 132.

Pure sodium chloride may be prepared by adding hydrochloric acid to a strong aqueous solution of salt; the sodium chloride is thereby precipitated, while the other salts remain in solution.

Sodium chloride forms colourless, cubical crystals, which are anhydrous. If deposited at − 10° it crystallises in monosymmetric prisms, with two molecules of water of crystallisation, which at the ordinary temperature lose their water, and break up into minute cubes.

Sodium chloride is a necessary article of food, for man and other animals; it is estimated that about 20 lbs. of salt per head of population is annually used, directly or indirectly, for this purpose. The hydrochloric acid present in the gastric and other acid fluids of the stomach, is derived from the decomposition of sodium chloride which is taken into the organism.

Enormous quantities of sodium chloride are employed in the alkali industry, and all the chlorine that is manufactured is derived primarily from this compound.

**Sodium Bromide**, NaBr, and **Sodium Iodide**, NaI, are prepared by methods similar to those for obtaining the potassium compounds. They are both isomorphous with sodium chloride, and when deposited at low temperatures they form monosymmetric crystals containing two molecules of water.

**Sodium Carbonate,** $Na_2CO_3$.—The preparation of this compound is carried on by two methods, and constitutes that important industry, the *alkali manufacture.* The two processes are known by the names of their respective discoverers, namely, the *Leblanc* process, and the *Solvay* process, the latter being also known as the *ammonia-soda* process.

I. The Leblanc method of manufacture consists essentially of three processes, namely—

(1.) The conversion of sodium chloride into sodium sulphate by the action of sulphuric acid, known as the *salt-cake* process. Two chemical reactions are involved in the process—

$$\begin{aligned} NaCl + H_2SO_4 &= NaHSO_4 + HCl. \\ NaCl + NaHSO_4 &= Na_2SO_4 + HCl. \end{aligned}$$

(2.) The decomposition of sodium sulphate, *salt-cake,* by means of calcium carbonate (limestone) and coal, at a high temperature, whereby a crude mixture of sodium carbonate and calcium sulphide is obtained, known as *black-ash.* This black-ash process takes place in accordance with the following equation—

$$Na_2SO_4 + CaCO_3 + 2C = Na_2CO_3 + CaS + 2CO_2.$$

The change may be conveniently regarded as taking place in two stages, which proceed simultaneously, according to the equations—

$$\begin{aligned} Na_2SO_4 + 4C &= Na_2S + 2CO_2. \\ Na_2S + CaCO_3 &= CaS + Na_2CO_3. \end{aligned}$$

(3.) The process of extracting and purifying the sodium carbonate contained in the *black-ash.*

(1.) *The Salt-cake Process.*—The first stage of this process is usually carried on in a large cast-iron pan (*D*, Fig. 132), built into a furnace in such a manner that it shall be heated as uniformly as possible. The charge of common salt is placed in the covered pan, and the requisite quantity of sulphuric acid is then run in. Hydrochloric acid is given off in torrents, according to the first of the above equations, and the gas is led away by the pipe *E* in the arched roof, to the condensing-towers, where it is absorbed by water (see Hydrochloric Acid, page 331). The mixture is heated until it begins to stiffen into a solid mass, when the damper *k* is raised, and the mass is raked out of the pan on to the hearth of the *roaster*, or reverberatory furnace, *b*. Here it is exposed to the hot gases from the coke fire *a*, which sweep over it, and ultimately raise its temperature nearly to a red heat, whereby the second of the above reactions is completed. The acid gas, together with the fire gases, leave the roaster by the chimney *e*, and are also led to condensing-towers, where the hydrochloric acid is absorbed. The mass is from time to time raked, or worked, by means of side-openings, or "working doors," in the roaster, and as soon as the operation is completed the salt-cake is withdrawn. The salt-cake so obtained, usually contains from 95 to 96 per cent. of normal sodium sulphate, $Na_2SO_4$; the remaining 4 or 5 per cent. consisting of hydrogen sodium sulphate, $NaHSO_4$, undecomposed sodium chloride, and such impurities as were originally present in the salt.

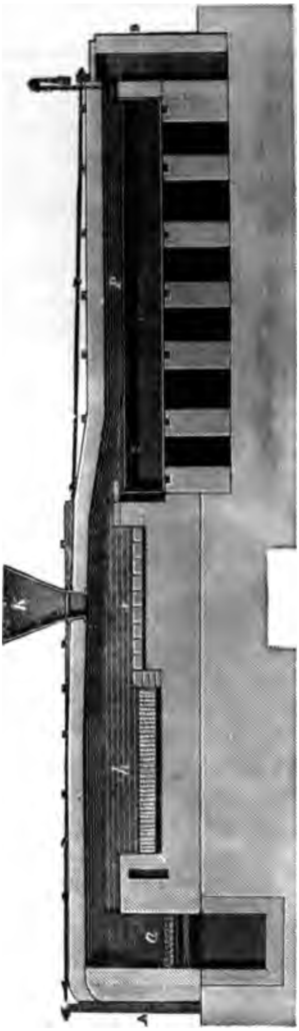

FIG. 133.

(2.) *The Black-ash Process.*—The salt-cake is mixed with limestone (or chalk) and coal dust (*slack*), and heated in a reverberatory furnace, known as the black-ash, or *balling*, furnace. As the mixture softens with the heat, it requires to be thoroughly mixed together, which, in the older forms of furnace (still used in many places), is accomplished by manual labour. Fig. 133 shows such a furnace in section. The materials are introduced by the hopper *k* on to the hearth *i*, where they are exposed to the hot gases from the fire *a*; and as the decomposition proceeds, they are raked along to the more strongly-heated front portion of the hearth *h*. During this process, carbon dioxide is freely evolved, the escaping bubbles of gas giving the semi-fluid mass the appearance of boiling. As the temperature rises, and the process approaches completion, the mass thickens, when it is worked up into large balls by means of rakes or *paddles*. At this stage, carbon monoxide begins to be evolved, the bubbles of which, bursting from the doughy material, become ignited and burn upon its surface as small jets of flame, coloured yellow by the soda. As soon as these appear, the ball is quickly withdrawn from the furnace. The formation of carbon monoxide, at the high temperature reached at this point in the process, is due to the action of carbon upon the limestone, according to the equation—

$$CaCO_3 + C = CaO + 2CO,$$

excess of these materials being intentionally present in the mixture. The effect of the escaping carbon monoxide at this point in the process, in rendering the black-ash light and porous (an important consideration in view of the next operation), is similar to that of baking-powder when used for cooking purposes. The heated gases from the furnace are made to pass over large evaporating pans, *P*, where liquors from a subsequent process are concentrated.

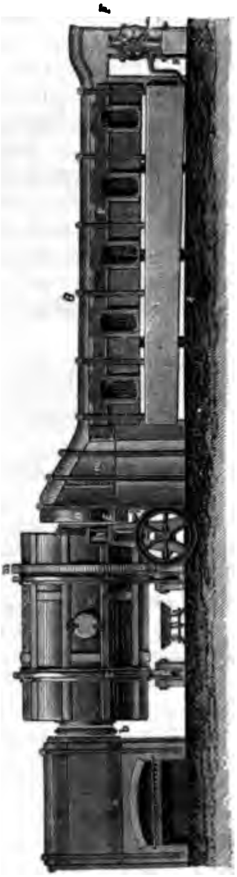

FIG. 134.

In the more modern forms of black-ash furnace, the mixing and working up of the materials is accomplished mechanically, by means of a revolving hearth. Fig. 134 shows the general arrangement of a revolving black-ash furnace. The mixture is placed in the cylinder *e*, which is made to slowly revolve upon its horizontal axis. The heated gases from the fire *a* pass through this revolving hearth; they are then conveyed through a dust-chamber, *m*, and finally over concentrating-pans. Limestone and two-thirds of the coal are first thrown into the furnace, and heated until the blue flame of burning carbon monoxide makes its appearance, when the salt-cake, along with the rest of the coal, is added, and the process continued until the yellow flames appear upon the surface of the mass. The contents of the cylinder are then thrown out into iron trucks beneath.

Black-ash is a mixture of variable composition, containing—

| | | | | | | |
|---|---|---|---|---|---|---|
| Sodium carbonate, $Na_2CO_3$ . | from | 40 | to | 45 | per cent. |
| Calcium sulphide, CaS . . | „ | 30 | „ | 33 | „ |
| Calcium carbonate, $CaCO_3$ . | „ | 6 | „ | 10 | „ |
| Coke . . . . . . | „ | 4 | „ | 7 | „ |
| Calcium oxide, CaO . . | „ | 2 | „ | 6 | „ |

And smaller quantities of sodium chloride, sodium sulphate, sodium sulphite, sodium sulphide, sodium thiosulphate, oxides of iron, alumina.

(3.) *Lixiviation of Black-ash.*—The lixiviation of black-ash is carried on in a series of tanks, so arranged that the liquid can be made to pass from one to the other. The action of water upon the black-ash is more than a simple process of dissolving the sodium carbonate from the mixture, for in the presence of water, chemical action takes place between some of the ingredients. Thus, the lime reacts upon sodium carbonate, forming sodium hydroxide, hence the *tank liquor* always contains caustic soda in varying quantities. Under certain conditions of temperature and dilution, the calcium sulphide also reacts upon the sodium carbonate, forming sodium sulphide and calcium carbonate, thus—

$$CaS + Na_2CO_3 = CaCO_3 + Na_2S.$$

Also by the oxidising influence of atmospheric oxygen, calcium sulphide, CaS, is converted into calcium sulphate, $CaSO_4$, which, in its turn, is acted upon by the sodium carbonate, involving loss of this product—

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$

The process of lixiviation is carried on as rapidly as possible, and at temperatures ranging from about 30° (for the dilute liquors) to about 60° (for those more concentrated); for the formation of sodium sulphide diminishes as the concentration of the liquid increases. The tank liquor, after settling, is then either at once concentrated by evaporation, when the soda crystallises out, leaving the caustic soda in the mother liquor, or it is submitted to the action of carbon dioxide, whereby both the caustic soda and the sodium sulphide are converted into sodium carbonate, thus—

$$2NaHO + CO_2 = Na_2CO_3 + H_2O.$$
$$Na_2S + CO_2 + H_2O = Na_2CO_3 + H_2S.$$

The concentration of the tank liquor is accomplished in the shallow pans above-mentioned, by means of the waste heat from the black-ash furnace; and the product obtained by evaporating the liquid, is usually calcined at a red heat in an ordinary reverberatory furnace. This substance is known as *soda-ash*, and when dissolved in water, and the solution allowed to crystallise, the so-called *soda crystals* are obtained, having the composition $Na_2CO_3,10H_2O$.

II. *The Ammonia-Soda Process.*—This process is based upon the fact, that hydrogen ammonium carbonate (*bicarbonate of ammonia*) is decomposed by a strong solution of sodium chloride, according to the equation—

$$H(NH_4)CO_3 + NaCl = HNaCO_3 + NH_4Cl.$$

In practice, the brine is first saturated with ammonia gas, and the cooled ammoniacal liquid is then charged with carbon dioxide, under moderate pressure, in carbonating towers.

The hydrogen sodium carbonate (*bicarbonate of soda*), being much less soluble, separates out, leaving the more soluble ammonium chloride in solution, from which the ammonia is recovered by subsequent treatment with lime.

The hydrogen sodium carbonate is converted into normal sodium carbonate by calcination, and the carbon dioxide evolved is again utilised in carbonating a further quantity of ammoniacal brine—

$$2HNaCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

Sodium carbonate crystallises in large, transparent, monosymmetric crystals, commonly known as "soda," or "washing-soda," having the composition $Na_2CO_3,10H_2O$. On exposure to the air, the crystals give up water, and become effloresced upon the surface, and finally fall to powder, having the composition $Na_2CO_3,H_2O$. When crystallised from hot solutions, it forms rhombic crystals, containing $7H_2O$. The solubility of sodium carbonate in water increases with rise of temperature, reaching a maximum of 32.5°, when 100 parts of water dissolve 59 parts of the salt. Above this temperature the solubility falls, and at 100° the amount dissolved is 45.4 parts.

**Hydrogen Sodium Carbonate** (*bicarbonate of soda*), $HNaCO_3$, may be obtained by the action of carbon dioxide upon the normal carbonate, either in solution, or as crystals –

$$Na_2CO_3,10H_2O + CO_2 = 2HNaCO_3 + 9H_2O.$$

The greater part of the bicarbonate of soda of commerce is obtained in the ammonia-soda process above described.

This salt is less soluble in water than the normal carbonate. Thus, 100 parts of water at different temperatures dissolves the following quantities of these compounds—

| | 10°. | 20°. | 30°. | 40°. |
|---|---|---|---|---|
| $Na_2CO_3$ . . . | 12.6 | 21.4 | 38.1 | 50 parts. |
| $HNaCO_3$ . . | 8.8 | 9.8 | 10.8 | 11.7 " |

When a solution of hydrogen sodium carbonate is heated, the salt gives off a portion of its carbon dioxide, and on cooling, the solution deposits crystals having the composition $Na_2CO_3,2HNaCO_3,2H_2O$, known as sodium sesquicarbonate. On continued boiling, the salt is completely converted into the normal carbonate. Sodium sesquicarbonate occurs as a natural deposit in Egypt, Africa, South America, and elsewhere, known as *trona*, from which the name *natrium* is derived.

**Sodium Sulphate** (*Glauber's salt*), $Na_2SO_4$, occurs native in the anhydrous condition as the mineral *thenardite*, and as a double sulphate of sodium and calcium, $Na_2SO_4,CaSO_4$, in the mineral *Glauberite*.

It is manufactured in immense quantities in the first (*salt-cake*) process in the alkali manufacture, by the Leblanc method.

It is also obtained in large supplies from the Stassfurt deposits, by double decomposition between magnesium sulphate (from *kieserite*) and sodium chloride.

The solution of the mixed salts, when cooled a few degrees below 0°, deposits sodium sulphate, and the soluble magnesium chloride remains in solution—

$$2NaCl + MgSO_4 = Na_2SO_4 + MgCl_2.$$

Sodium sulphate is also manufactured by the action of sulphur dioxide and oxygen upon sodium chloride. This is known as *Hargreave's process.* The reaction is expressed by the equation—

$$2NaCl + SO_2 + O + H_2O = Na_2SO_4 + 2HCl.$$

This process is, in essence, the production of sodium sulphate from sodium chloride, and the *constituents of sulphuric acid*, without the intermediate manufacture of the acid. The gases from pyrites burners, similar to those used by the "vitriol" manufacturer, together with steam, are passed through a series of cast-iron cylinders containing sodium chloride, and maintained at a temperature of 500° to 550°. Many days are required for the complete conversion of the chloride into sulphate by this process.

Sodium sulphate crystallises in colourless prisms belonging to the monosymmetric system, containing ten molecules of water: when exposed to the air the crystals effloresce, and when heated to 33°, they melt in their own water of crystallisation (see page 132).

When sodium sulphate is heated with sulphuric acid, in the proportions required by the following equation, hydrogen sodium sulphate is formed—

$$Na_2SO_4 + H_2SO_4 = 2HNaSO_4.$$

**Sodium Nitrate,** $NaNO_3$, occurs associated with other salts, in Bolivia and Peru, as *cubical nitre*, or *Chili saltpetre*. The crude salt is purified by solution in water, and crystallisation. It forms rhombohedral crystals, isomorphous with calcspar. 3

Sodium nitrate is very soluble in water. 100 parts of water dissolve at 0°, 68.8 parts; at 40°, 102 parts; and at 100°, 180 parts, of the salt. When exposed to the air, the salt absorbs moisture, and on this account cannot be employed as a substitute for potassium nitrate in the manufacture of gunpowder, or in pyrotechny. Its chief uses are for the manufacture of nitric acid; for the manufacture of potassium nitrate by double decomposition with potassium chloride; and as an ingredient in artificial manures.

**Sodium Phosphates.**—The most important of these compounds is the hydrogen disodium orthophosphate, or common *phosphate of soda*, $HNa_2PO_4$. This salt is prepared on a large scale, by adding sodium carbonate to phosphoric acid until the solution is alkaline, and then filtering and evaporating the solution, when large transparent prisms, belonging to the monosymmetric system, are deposited, having the composition $HNa_2PO_4,12H_2O$. Exposed to the air the crystals effloresce, and when heated become anhydrous. The salt melts at 35°.

One hundred parts of water at 10° dissolve 4.1 parts; at 50°, 43.3 parts; and at 100°, 108.2 parts, of the anhydrous salt.

**Normal Sodium Orthophosphate,** $Na_3PO_4$, is obtained from hydrogen disodium phosphate, by evaporating a solution of the latter salt with sodium hydroxide, until the liquid crystallises—

$$HNa_2PO_4 + NaHO = Na_3PO_4 + H_2O.$$

This salt contains twelve molecules of water, and forms thin six-sided prisms. Its aqueous solution is strongly alkaline, and absorbs atmospheric carbon dioxide, with the formation of sodium carbonate and hydrogen disodium phosphate, thus—

$$Na_3PO_4 + CO_2 + H_2O = HNa_2PO_4 + HNaCO_3.$$

**Dihydrogen Sodium Orthophosphate,** $H_2NaPO_4$, is obtained when phosphoric acid is added to ordinary phosphate of soda, until the liquid gives no precipitate with barium chloride. On evaporating the solution, the salt crystallises.

$$HNa_2PO_4 + H_3PO_4 = 2H_2NaPO_4.$$

The aqueous solution of this salt is acid.

**Hydrogen Sodium Ammonium Phosphate** (*microcosmic salt*), $HNa(NH_4)PO_4$, is obtained by adding a strong solution of common sodium phosphate to ammonium chloride—

$$HNa_2PO_4 + NH_4Cl = NaCl + HNa(NH_4)PO_4.$$

The orthophosphates are readily converted into pyro- and metaphosphates (see page 436).

## LITHIUM.

Symbol, Li. Atomic weight = 7.01.

**rrence.**—Lithium is only found in combination with other s. It is a constituent of a few somewhat rare minerals, as $30SiO_2,4Al_2O_3,Na_2O,2Li_2O$ ; *spodumene*, $15SiO_2,4Al_2O_3$, *lepidolite*, or *lithium mica*, $9SiO_2,3Al_2O_3,K_2O,4LiF$. 
ıeans of the spectroscope, lithium compounds have been 1 in sea water, and in most spring and river waters. In a es spring waters are met with which contain considerable es of lithium salts. Thus, W. A. Miller found as much as ramme of lithium chloride in 1 litre of the water of a spring druth in Cornwall.

**of Formation.**—Lithium is obtained by the electrolytic osition of the fused chloride. For this purpose the dry ıeated in a porcelain crucible, when it melts at a low red a mobile liquid. A rod of *gas carbon* is made the positive le ; and a stout iron wire, one end of which is flattened out, for the negative pole, upon which the lithium is collected. sing an electric current through the molten chloride, the orms as a bright globule upon the negative electrode. The withdrawn and quickly dipped beneath petroleum, and the d globule of lithium is then cut off with a knife. The l metal, in its passage from the crucible to the petroleum, ected from oxidation by the film of fused chloride which

**erties.**—Lithium is a soft, silver-white metal, which soon es on exposure to the air. It is easily cut with a knife, ofter than lead, but harder than sodium. It may be pressed re, and two pieces of the metal may be made to adhere, ed together, at the ordinary temperature. Lithium is the known solid, its specific gravity being 0.59. Its extreme ss is illustrated by the fact that the metal floats upon ım, a liquid which itself floats upon water. Lithium melts and at a higher temperature it takes fire and burns with t white light. Lithium decomposes water at the ordinary ature, liberating hydrogen and forming lithium hydroxide, but when a fragment of the metal is thrown upon cold : does not melt, and even with boiling water the action is nded by inflammation of the hydrogen.

When strongly heated in nitrogen the two elements unite, with feeble combustion, forming lithium nitride, $NLi_3$.

**Lithium Oxide,** $Li_2O$, is formed when the metal burns in the air. It is also obtained by heating the nitrate. It dissolves in water, forming lithium hydroxide, $LiHO$.

**Lithium Hydroxide** is produced by the prolonged boiling of lithium carbonate with milk of lime, the carbonate of this metal, unlike potassium and sodium carbonates, being only very slightly soluble in water.

**Lithium Carbonate,** $Li_2CO_3$, is obtained as a white precipitate when a solution of either potassium, sodium, or ammonium carbonate is added to a solution of either chloride or nitrate of lithium. The compound is only slightly soluble in cold water, 100 parts of water at 13° dissolving 0.77 parts of the carbonate.

**Lithium Phosphate,** $Li_3PO_4$, is precipitated as a crystalline powder, by the addition of hydrogen disodium phosphate to a solution of a lithium salt. In the presence of sodium hydroxide the precipitation is complete, and the formation of this compound is employed as a quantitative method for estimating lithium. The crystals contain $2H_2O$, which they lose when heated. Lithium phosphate is soluble in nitric, hydrochloric, and phosphoric acids, and from the latter solution, on evaporation, the dihydrogen phosphate is deposited ($H_2LiPO_4$), as deliquescent, and very soluble crystals. The chloride, nitrate, and sulphate of lithium are obtained by dissolving the carbonate in the respective acids. The salts are readily soluble in water.

**Rubidium and Caesium.**[*]—These two rare elements, which were first discovered by Bunsen in the waters of Dürkheim, in the years 1860–61, are met with, associated with sodium and potassium, in certain minerals, such as lepidolites (lithium mica), porphyrites, and in carnallite. They are also found in many mineral waters, in the mother liquors from the evaporation of sea water, and in the ashes of plants. Although widely distributed, the quantities present are extremely minute, one of the richest lepidolites in which these metals occur, containing only 0.24 per cent. of rubidium oxide.

The rare mineral *pollux*, a silicate of aluminium and caesium, containing also iron calcium and sodium, is the only known mineral in which either of these two elements occurs as an essential constituent. The analysis of Pisani (1864) gives 34.07 per cent. of caesium oxide in this substance.

Rubidium is obtained by heating the carbonate with carbon (the charred tartrate), as in the older method for the preparation of sodium and potassium.

---

[*] For detailed descriptions of these elements and their compounds, the student is referred to larger works.

Caesium cannot be isolated by this reaction, but is obtained by the electrolysis of the fused cyanide, $Cs(CN)$ (mixed with barium cyanide in order to render it more readily fusible). Rubidium melts at 38.5, caesium at 26.5.

Rubidium gives a green vapour, and when sublimed in a vacuous tube yields a thin film of metal, which appears deep blue by transmitted light: when slowly sublimed in this way the metal forms small needle-shaped crystals. The compounds of these metals closely resemble those of potassium, from which they can only be distinguished by the different spectra they give.

## AMMONIUM SALTS.

The monovalent group or radical ($NH_4$) is capable of replacing one atom of hydrogen in acids, thereby giving rise to a series of salts which are closely analogous to, and are isomorphous with, those of potassium. The radical ($NH_4$), to which the name *ammonium* is given, has never been isolated. When an amalgam of sodium and mercury is thrown into a solution of ammonium chloride, the mercury swells up into a honeycombed or sponge-like mass, which floats upon the surface of the liquid. This so-called ammonium amalgam was at one time thought to be a true amalgam of mercury with the metallic radical ammonium. It is now generally believed to consist of mercury which is simply inflated by the evolution of hydrogen and ammonia gas. When this sponge-like substance is subjected to changes of pressure, it is found to contract and expand in conformity to Boyle's law: its formation may be represented by the equation—

$$Hg_xNa_y + yNH_4Cl = yNaCl + xHg + yNH_3 + yH.$$

In the course of a few minutes the inflated mass shrinks down, and ordinary mercury remains at the bottom of the solution, hydrogen and ammonia having been rapidly evolved.

The ammonium salts are obtained for the most part from the *ammoniacal liquor* of the gasworks. This material is treated with lime, and distilled; and the ammonia so driven off is absorbed in sulphuric or hydrochloric acid, giving rise to ammonium sulphate or chloride.

**Ammonium Chloride** (*sal ammoniac*), $NH_4Cl$.—The product obtained by absorbing ammonia from gas liquor in hydrochloric acid, is purified by sublimation. The crude material is heated in large iron pots, covered with iron dome-shaped vessels, into which the substance sublimes. Ammonium chloride crystallises in arborescent or fern-like crystals (Fig. 135), consisting of groups of small octahedra belonging to the regular system.

100 parts of water at 10° dissolve 32.8 parts, and at 100°, 77 parts of the salt. On boiling the aqueous solution, dissociation to a small extent takes place, and a portion of the ammonia escapes with the steam; the solution at the same time becoming slightly acid.

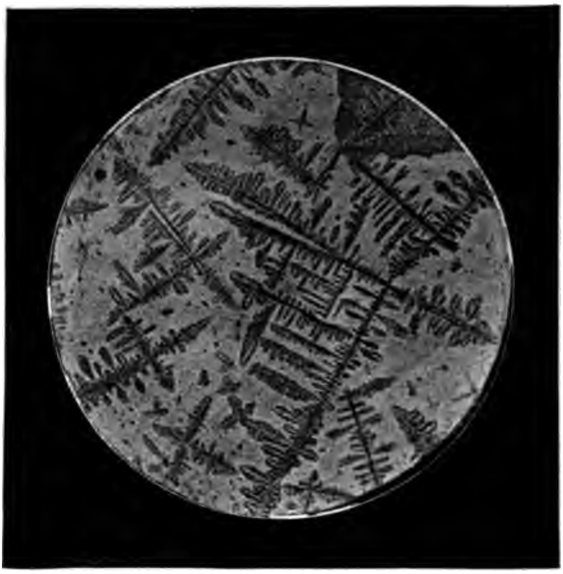

FIG. 135.

**Ammonium Sulphate** $(NH_4)_2SO_4$.—The product obtained by the absorption of ammonia obtained from gas liquors, by sulphuric acid, is purified by recrystallisation, when it forms colourless rhombic crystals, isomorphous with potassium sulphate. 100 parts of water at the ordinary temperature dissolve 50 parts of the salt. The chief use of ammonium sulphate is for agricultural purposes, as a manure; and for this use the crude salt, as first obtained, which is usually more or less coloured with tarry matters, is employed. Ammonium sulphate is also used for the preparation of ammonia alum, and other ammonium compounds, as well as in the ammonia-soda process.

**Ammonium Carbonates.**—Commercial ammonium carbonate (*sal volatile*) is obtained, by heating a mixture of ammonium sulphate and ground chalk to redness in horizontal iron retorts or cylinders, and conducting the vapours into leaden receivers or chambers, where the carbonate condenses as a solid crust. It is afterwards purified by resublimation, when it is obtained as a white fibrous mass. This substance is a mixture of hydrogen ammonium carbonate, $H(NH_4)CO_3$, and ammonium carbamate $(NH_4)CO_2(NH_2)$, and smells strongly ammoniacal. When treated with alcohol the ammonium carbamate is dissolved, leaving the carbonate behind.

**Normal Ammonium Carbonate,** $(NH_4)_2CO_3$, is obtained from the commercial compound, by passing ammonia gas into a strong aqueous solution, or by digesting the compound in strong aqueous ammonia. The carbamate present is converted into normal carbonate by the action of the water, thus—

$$(NH_4)CO_2(NH_2) + H_2O = (NH_4)CO_3(NH_4) = (NH_4)_2CO_3 ;$$

and the ammonia converts the bicarbonate into the normal salt, thus—

$$H(NH_4)CO_3 + NH_3 = (NH_4)_2CO_3.$$

Normal ammonium carbonate on exposure to the air gives off ammonia, and passes back into hydrogen ammonium carbonate. When heated to 60° the salt breaks up into carbon dioxide, ammonia, and water.

**Hydrogen Ammonium Carbonate,** $H(NH_4)CO_3$, may also be obtained by passing carbon dioxide into a solution of the normal salt—

$$(NH_4)_2CO_3 + CO_2 + H_2O = 2H(NH_4)CO_3.$$

It forms large lustrous crystals belonging to the rhombic system, which, when dry, do not smell of ammonia. 100 parts of water at 15° dissolve 12.5 parts of this salt. At ordinary temperatures this solution on exposure to the air slowly gives off carbon dioxide, and becomes alkaline; and when heated above 36° the liquid begins to effervesce, owing to the rapid evolution of carbon dioxide. This salt forms with the normal carbonate a double salt, analogous to sodium sesquicarbonate, and having the composition $(NH_4)_2CO_3$, $2H(NH_4)CO_3$, $H_2O$.

**Ammonium Thiocyanate,** $NH_4S(CN)$, is prepared by adding aqueous ammonia to an alcoholic solution of carbon disulphide, and allowing the mixture to stand, when ammonium thiocarbonate is formed, thus—

$$6NH_3 + 3H_2O + 3CS_2 = 2(NH_4)_2CS_3 + (NH_4)_2CO_3.$$

On heating this solution, the ammonium thiocarbonate is decomposed with evolution of sulphuretted hydrogen—

$$(NH_4)_2CS_3 = 2H_2S + NH_4S(CN).$$

Ammonium thiocyanate (known also as *ammonium sulphocyanate*) forms colourless crystals, which are extremely soluble both in water and alcohol. The solution in water is attended with considerable absorption of heat: thus, if 20 grammes of the salt be dissolved in 25 cubic centimetres of water at 18°, the temperature of the liquid falls to − 13°.

# CHAPTER V

## *THE ELEMENTS OF GROUP I. (FAMILY B.)*

| | |
|---|---|
| Copper, Cu | 63.18 |
| Silver, Ag | 107.66 |
| Gold, Au | 196.8 |

THE elements of this family present many striking contrasts to those of the other family belonging to the first group. These three metals are not acted upon by oxygen, or by water, at ordinary temperatures; they are all found native in the uncombined state, and on this account are amongst the earliest metals known to man. The alkali metals, on the other hand, are instantly oxidised on exposure to air, they decompose water at the ordinary temperature, are never found native, and are amongst the most recently discovered metals. With the exception of sodium and potassium, which are used in a few manufacturing processes, the alkali metals, as such, are of little practical service to mankind, whilst the metals of this family are amongst the most useful of all the metals, and are the three universally adopted for coinage. Many of the compounds of the elements of this family, are similarly constituted to those of the alkali metals: thus, with oxygen and with sulphur we have $Cu_2O$, $Ag_2O$, $Au_2O$, and $Cu_2S$, $Ag_2S$, $Au_2S$, corresponding to $K_2O$ and $K_2S$.

With the halogens they all form compounds of the type RX. Although the three elements, copper, silver, and gold, fall into the same family, upon the basis of the periodic classification of the elements, they are in many respects widely dissimilar. Thus, silver is consistently monovalent, while copper is divalent, forming compounds of the type $CuX_2$, and gold is trivalent, giving compounds $AuX_3$. The chlorides, AgCl and $Cu_2Cl_2$, on the other hand, are both insoluble in water, are both soluble in ammonia, and both absorb ammonia.

In many of their physical attributes, these metals show a regular gradation in their properties. Thus, as regards malleability and ductility, silver is intermediate between copper and gold, the latter possessing these properties in the highest degree. With respect to their tenacity, silver is again intermediate, copper being the most, and gold the least tenacious of the three.

## COPPER.

Symbol, Cu. Atomic weight = 63.18.

**Occurrence.**—Copper is found in the elementary condition in various parts of the world, notably in the neighbourhood of Lake Superior, where native copper occurs in enormous masses. In combination, copper is a very abundant element, and is widely distributed, the most important of these natural compounds being the following—

| | | | |
|---|---|---|---|
| Ruby ore . . . | $Cu_2O$. | Purple copper ore | $3Cu_2S,Fe_2S_3$. |
| Copper glance . . | $Cu_2S$. | Malachite . . | $CuCO_3,Cu(HO)_2$. |
| Copper pyrites . . | $Cu_2S,Fe_2S_3$. | Azurite . . | $2CuCO_3,Cu(HO)_2$. |

**Modes of Formation.**—The methods by which copper is obtained from its ores, vary with the nature of the ore. From ores containing no sulphur, such as the carbonates and oxide, the metal may be obtained by a method known as the *reducing process*, which consists in smelting down the ore in a blast-furnace with coal or coke, when the metal is reduced according to the equation—

$$Cu_2O + C = CO + 2Cu.$$

In the case of mixed ores, containing sulphides, the process (known as the English method) consists of six distinct stages—

(1.) The ores, which contain on an average 30 per cent. of iron and 13 of copper (the remainder being chiefly sulphur and silica), are first calcined; usually in a reverberatory furnace, whereby a portion of the sulphur is burnt to sulphur dioxide, and the metals are partially oxidised.

(2.) The second step consists in fusing the calcined ore; when the copper oxides, formed during calcination, react upon a portion of the ferrous sulphide with the formation of cuprous sulphide and ferrous oxide, thus—

$$Cu_2O + FeS = Cu_2S + FeO.$$
$$2CuO + 2FeS = Cu_2S + 2FeO + S.$$

The oxide of iron combines with the silica already present (or which is added in the form of *metal slag* obtained from the fourth process) to form a fusible silicate of iron, or slag, which contains little or no copper. This is run off, and a fused regulus remains, consisting of cuprous and ferrous sulphides, known as *coarse-metal*, and containing from 30 to 35 per cent. of copper. This molten regulus, which has a composition very similar to copper pyrites, is usually allowed to flow into water, whereby it is obtained in a granulated condition favourable for the next operation.

(3.) The third step consists in calcining the granulated coarse-metal; the result, as in the first calcination, being the removal of a part of the sulphur as sulphur dioxide, and the partial oxidation of the metals.

(4.) The calcined mass is next fused along with *refinery-slag*, which results in the production of a regulus consisting of nearly pure cuprous sulphide, the greater part of the iron having passed into the slag (known as *metal-slag*). This regulus, called *fine-metal*, or *white-metal*, contains from 60 to 75 per cent. of copper.

(5.) The fifth operation consists in roasting the "white-metal" in a reverberatory furnace. A portion of the cuprous sulphide is here oxidised into cuprous oxide, which, as the temperature rises, reacts upon another portion of cuprous sulphide, thus—

$$2Cu_2O + Cu_2S = 6Cu + SO_2.$$

At the same time any remaining ferrous sulphide is converted into oxide, thus—

$$3Cu_2O + FeS = 6Cu + FeO + SO_2.$$

The metallic copper so obtained, presents a blistered appearance, and on this account is known as *blister-copper*.

(6.) This impure copper is lastly subjected to a refining process. For this purpose it is melted down upon the hearth of a reverberatory furnace, in an oxidising atmosphere. The impurities present in the metal, such as iron, lead, and arsenic, are the first to oxidise; and the oxides either volatilise, or combine with the siliceous matter of which the furnace bed is composed, forming a slag, which is removed. The oxidation is continued until the copper itself begins to oxidise, when the oxide so formed reacts upon any remaining cuprous sulphide with the reduction of copper and the evolution of sulphur dioxide, according to the above equation. The metal at this stage is termed *dry copper;* and in order to reduce the copper oxide which it still contains, the molten mass is stirred with poles of wood, and a quantity of anthracite is thrown upon the surface to complete the reducing process.

**Wet Process.**—Copper is extracted from the burnt pyrites, obtained in enormous quantities in the manufacture of sulphuric acid, which contains about 3 per cent. of copper. Although too poor in copper to be submitted to the smelting process, it is found that when calcined with 12 to 15 per cent. of common salt, the copper is all converted into cupric chloride. On lixiviating the calcined mass with water, the cupric chloride goes into solution, and metallic copper can be precipitated from it by means of scrap-iron.

**Properties.**—Copper is a lustrous metal, having a characteristic reddish-brown colour. The peculiar copper-red colour of the metal is best seen, by causing the light to be several times reflected from the surface before reaching the eye.

Native copper is occasionally found crystallised in regular octahedra, and small crystals of the same form may be artificially obtained, by the slow deposition of the metal from solutions of its salts by processes of reduction.

Copper is an extremely tough metal, and admits of being drawn into fine wire, and hammered out into thin leaf. Its ductility and malleability are greatly diminished by admixture with even minute quantities of impurities. When heated nearly to its melting-point, copper becomes sufficiently brittle to be powdered. The specific gravity of pure copper, electrolytically deposited, is 8.945, which by hammering is increased to 8.95.

Copper is only slowly acted upon by exposure to dry air at ordinary temperatures; but in the presence of atmospheric moisture and carbon dioxide, it becomes coated with a greenish basic carbonate. When heated in air or oxygen, it is converted into black cupric oxide, which flakes off the surface in the form of scales. When volatilised in the electric arc, copper gives a vapour having a rich emerald green colour.

Copper is readily attacked by nitric acid, either dilute or concentrated, with the formation of copper nitrate and oxides of nitrogen (page 221).

Dilute hydrochloric and sulphuric acids are without action upon copper when air is excluded, but slowly attack it in the presence of air, or in contact with platinum. Cold concentrated sulphuric acid does not act upon copper; but, when heated, copper sulphate and sulphur dioxide are formed (page 377).

divided copper is slowly dissolved by boiling concen-
lrochloric acid, with evolution of hydrogen and formation
ı chloride :—

$$2Cu + 2HCl = Cu_2Cl_2 + H_2.$$

presence of air, copper is acted upon by a solution of
the oxide dissolving in the ammonia forming a deep
ion.

is an extremely good electric conductor, being only
ı silver in this respect; it is therefore extensively em-
r cables, or leads, for purposes of telegraphy and electric

possesses the property, in a high degree, of being de-
ı a coherent form by the electrolysis of solutions of its
ı this account it is extensively used in processes of
ing.

**of Copper.**—The most extensive use of copper is in
tion of certain alloys, many of which are of great technical
he following are among the most important :—

| | | | | | | |
|---|---|---|---|---|---|---|
| ı brass . . . | Copper | 2 | parts | Zinc | 1 | part |
| brass (*Tombac*) . | „ | 5 | „ | „ | 1 | „ |
| metal . . . | „ | 3 | „ | „ | 1 | „ |
| etal . . . | „ | 9 | „ | Tin | 1 | „ |
| ium bronze . . | „ | 9 | „ | Aluminium | 1 | „ |

**of Copper.**—Two oxides of copper are well known,
uprous oxide (*copper sub-oxide*), $Cu_2O$, and cupric oxide
*onoxide*), CuO.

**is Oxide**, $Cu_2O$, occurs native as *red copper ore.* It is
hen finely divided copper is gently heated in a current
when a mixture of cuprous chloride and sodium carbonate
heated in a covered crucible.

$$Cu_2Cl_2 + Na_2CO_3 = 2NaCl + CO_2 + Cu_2O.$$

is oxide is also obtained when an alkaline solution of a
lt is reduced by grape sugar.

is oxide is insoluble in water ; it is converted into cuprous
by strong hydrochloric acid. Nitric acid converts it into

cupric nitrate with the evolution of oxides of nitrogen. When acted upon by dilute sulphuric acid, it is partly reduced to metallic copper, and partly oxidised into copper sulphate, thus—

$$Cu_2O + H_2SO_4 = CuSO_4 + Cu + H_2O.$$

When heated with the strong acid it is entirely oxidised, thus—

$$Cu_2O + 3H_2SO_4 = 2CuSO_4 + SO_2 + 3H_2O.$$

Cuprous oxide fuses at a red heat, and when melted with glass, imparts to the latter a rich ruby-red colour.

**Cupric Oxide,** $CuO$, occurs as the rather rare mineral, *tenorite.* It is formed when copper is strongly heated in the air or in oxygen, or by gently igniting either the nitrate, carbonate, or hydroxide. It is a black powder, which rapidly absorbs moisture from the air. When heated, it first cakes together and finally fuses, giving up a part of its oxygen, and leaving a residue consisting of $CuO,2Cu_2O$.

When heated in a stream of carbon monoxide, marsh gas, or hydrogen, it is reduced to the metallic state. Similarly, when mixed with organic compounds containing carbon and hydrogen, it oxidises these elements to carbon dioxide and water, itself being reduced: on this property depends its use in the ultimate analysis of organic compounds.

**Cupric Hydroxide,** $Cu(HO)_2$, is the pale blue precipitate produced when sodium or potassium hydroxide is added in excess to a solution of a copper salt. The compound, when washed, may be dried at 100° without parting with water; but if the liquid in which it is precipitated be boiled, the compound blackens, and is converted into a hydrate having the composition $Cu(HO)_2,2CuO$. Cuprous hydrate dissolves in ammonia, forming a deep blue liquid, which possesses the property of dissolving cellulose (cotton wool, filter paper, &c.)

**Salts of Copper.**—Copper forms two series of salts, namely, *cuprous* and *cupric* salts. The former, which are colourless, readily pass by oxidation into cupric salts, and serve therefore as powerful reducing agents, and are mostly insoluble in water. The cupric salts in the hydrated condition, are either blue or green in colour; the anhydrous cupric salts are colourless or yellow. The normal salts are mostly soluble in water. Copper salts impart to a non-luminous flame a blue or green colour, and on this account are employed in pyrotechny. The soluble salts are poisonous.

**Cuprous Chloride,** $Cu_2Cl_2$, may be obtained by dissolving cuprous oxide in hydrochloric acid. It is more readily prepared by boiling a solution of cupric chloride in hydrochloric acid, with copper turnings or foil. The nascent hydrogen, liberated by the action of the hydrochloric acid upon the copper, reduces the cupric chloride to cuprous chloride. The liquid is then poured into water, which causes the precipitation of the cuprous chloride as a white crystalline powder.

A mixture of zinc dust and copper oxide added to strong hydrochloric acid, also yields cuprous chloride, the nascent hydrogen in this case being derived from the action of the acid upon the zinc, and this causes the reduction of cupric chloride formed by the action of the acid upon the cupric oxide.

Cuprous chloride melts when heated, and volatilises without decomposition. It is insoluble in water, but dissolves in hydrochloric acid, ammonia, and alkaline chlorides. These solutions, on exposure to the air, absorb oxygen, turning first brown, and finally depositing a greenish-blue precipitate of copper oxychloride, $CuCl_2,3CuO,4H_2O$. This compound occurs native as the mineral *atacamite*. Solutions of cuprous chloride also absorb carbon monoxide, forming a crystalline compound, believed to have the composition, $COCu_2Cl_2,2H_2O$. They also absorb acetylene (see page 280).

Cuprous bromide, $Cu_2Br_2$; iodide, $Cu_2I_2$; and fluoride, $Cu_2F_2$, are also known.

**Cupric Chloride,** $CuCl_2$.—This compound is formed when copper is dissolved in nitro-hydrochloric acid, or when cupric oxide, carbonate, or hydroxide, are dissolved in hydrochloric acid. It is also produced when copper is burnt in chlorine.

Cupric chloride is readily soluble in water, forming a deep green solution, which, on being largely diluted, turns blue. The salt crystallises in green rhombic prisms, with $2H_2O$. When heated, it loses its water, and at a dull red heat is converted into cuprous chloride, with evolution of chlorine (see page 317).

Cupric chloride forms three compounds with ammonia. The anhydrous salt absorbs ammonia gas, forming a blue compound, $CuCl_2,6NH_3$. When ammonia is passed into aqueous cupric chloride, the solution deposits deep blue quadratic octahedral crystals of the compound, $CuCl_2,4NH_3,H_2O$. Both these substances, when moderately heated, yield the green compound $CuCl_2,2NH_3$, which at a higher temperature is decomposed, thus—

$$6(CuCl_2,2NH_3) = 3Cu_2Cl_2 + 6NH_4Cl + 4NH_3 + N_2.$$

Cupric bromide, $CuBr_2$, and fluoride, $CuF_2$, are known, but the iodide is unknown.

**Cupric Nitrate,** $Cu(NO_3)_2,3H_2O$, may be obtained by the action of nitric acid upon cupric oxide, hydroxide, carbonate, or the metal itself. It is deposited from the solution in deep blue deliquescent crystals, soluble in alcohol. When heated to about 65°, the crystals lose nitric acid and water, and are converted into the basic nitrate, $Cu(NO_3)_2,3Cu(HO)_2$. The normal salt, therefore, cannot be obtained anhydrous. Cupric nitrate is a caustic, powerfully oxidising substance. If the moist salt be rubbed in a mortar with a quantity of tinfoil, the tin is quickly converted into oxide, with considerable rise of temperature. When a solution containing copper nitrate and ammonium nitrate is evaporated, the mixture suddenly deflagrates when a certain degree of concentration is reached.

**Cupric Sulphate** (*blue vitriol*), $CuSO_4,5H_2O$, is the most important of all the copper salts. It is formed when either the metal or the oxide is dissolved in sulphuric acid. On a commercial scale, it is obtained from waste copper by first converting the metal into sulphide, by heating it in a furnace, and throwing sulphur upon the red-hot metal. Air is then admitted, and the sulphide is thereby oxidised into sulphate, which is dissolved in water, and crystallised.

It is also manufactured from the sulphur ores of copper, by roasting them under such conditions that the iron is for the most part converted into oxide, while the copper is oxidised to sulphate. On lixiviating the roasted mass, the copper sulphate, with a certain amount of ferrous sulphate, is dissolved out. The ores may also be roasted so as to convert both the metals into oxides; the mass is then treated with "chamber acid," which dissolves copper oxide, leaving the iron oxide for the most part unacted upon.

Cupric and ferrous sulphates cannot be entirely separated by crystallisation, as a solution of these salts deposits a double sulphate of the two metals. If, however, the amount of iron present is comparatively small, the first crop of crystals obtained, is ly pure copper sulphate. The copper is removed from er liquors by precipitation upon plates of iron, and the obtained is converted into sulphide, as above described. sulphate forms large blue asymmetric (*triclinic*) crystals, O. At 100° it is converted into a bluish-white salt, $_2$O, and at 220° to 240° it becomes anhydrous. The s salt is white, and extremely hygroscopic, and is used the detection and removal of small quantities of water c liquids.

ındred parts of water at 10° dissolve 36.6 parts, and at 3 parts, of the crystallised salt.

l basic sulphates of copper are known: thus, when the ılt is submitted to prolonged heating, it is converted into ›hous yellow powder, consisting of $CuSO_4,CuO$, which, own into cold water, forms an insoluble green compound, Cu(HO)$_2$, and on treatment with boiling water yields Cu(HO)$_2$. Copper sulphate forms several compounds ıonia. Thus, the anhydrous salt readily absorbs ammonia ning the compound, $CuSO_4,5NH_3$. When excess of is added to a solution of copper sulphate, the deep blue deposits blue crystals of $CuSo_4,H_2O,4NH_3$. At 150° pound is converted into $CuSO_4,2NH_3$, and at 200° it more molecule of ammonia, leaving $CuSO_4,NH_3$.

**Carbonates.**—The normal carbonate has not been The two most important basic carbonates are (1) u(HO)$_2$, occurring native as *malachite*, and obtained when :arbonate is added to a solution of copper sulphate (the posit which appears upon copper, when exposed to atmos-oisture and carbon dioxide (*verdigris*), is the same com-and (2) $2CuCO_3,Cu(HO)_2$, occurring as the mineral *azurite*.

**ldes of Copper.**—Two sulphides are known, correspond-e two oxides.

*us sulphide*, $Cu_2S$, occurs in nature as *copper glance*, orm of grey metallic-looking rhombic crystals. It is l when copper burns in sulphur vapour, or when an copper filings is heated with sulphur.

*Sulphide*, CuS, is met with in nature as the mineral *indigo-* It is obtained when either copper or cuprous sulphide is ith sulphur to a temperature not beyond 114°; so obtained, ›ound is blue. As a black precipitate, it is formed when tted hydrogen is passed into solutions of cupric salts.

## SILVER.

Symbol, Ag. Atomic weight = 107.66.

**Occurrence.** — Silver is found uncombined, occasionally in masses weighing several cwts. Such native silver usually contains copper, gold, and other metals.

Amongst the more important natural compounds of silver are the following :—

| | |
|---|---|
| Argentite, or *silver glance* | $Ag_2S$. |
| Pyrargyrite, or *ruby silver ore* | $3Ag_2S,Sb_2S_3$, or $Ag_3SbS_3$ |
| Proustite, or *light-red silver ore* | $3Ag_2S,As_2S_3$ „ $Ag_3AsS_3$ |
| Stephanite | $5Ag_2S,Sb_2S_3$ „ $Ag_5SbS_4$ |
| Polybasite | $9(Ag_2S,Cu_2S),Sb_2S_3,As_2S_3$ |
| Stromeyerite | $Ag_2S,Cu_2S$. |
| Horn silver | $AgCl$. |

Silver is present also in most ores of lead, notably with *galena* (lead sulphide); argentiferous lead ores constituting one of the main supplies of silver.

**Modes of Formation.**—This element may be obtained from its salts by the electrolysis of their aqueous solutions. The metal is so readily reduced from its compounds, that many organic substances, such as grape sugar, aldehyde, certain tartrates, &c., are capable of effecting its deposition. When a strip of zinc is introduced into silver nitrate solution, the silver is at once deposited upon the zinc as a crystalline mass.

Pure silver for analytical purposes may be prepared by precipitating silver chloride, by the addition of hydrochloric acid to a solution of the nitrate, and reducing the chloride by boiling with sodium hydroxide and sugar, or by means of metallic zinc. In this way the metal is obtained as a fine grey powder. The chloride may also be reduced by fusion with sodium carbonate, when the silver is obtained as a button at the bottom of the crucible. The methods by which silver is obtained from its ores are very varied; they may, however, be classed under three heads, namely—

1. Processes involving the use of mercury. (Amalgamation processes.)
2. Processes by means of lead.

3. Wet processes.

(1.) **Amalgamation Processes.**—These depend upon the fact that certain compounds of silver are reduced by mercury. The reduced silver then dissolves in the mercury, forming an amalgam, from which the silver is obtained, and the mercury recovered by distillation. The process, as still carried on in Mexico and South America, is the following. The ore is first crushed and then ground to a fine powder with water, and the mud so obtained is mixed with 3 to 5 per cent. of common salt, and spread upon the floor of a circular paved space, the mixing being effected by the treading of mules. After the lapse of a day, mercury is added, together with a quantity of roasted pyrites (known as *magistral*, and consisting of a crude mixture of cupric and ferric sulphates and oxides), and the materials thoroughly incorporated. Fresh mercury is added from time to time, during the several days required for the completion of the chemical decompositions that take place. The exact nature of these changes is not thoroughly understood, but it is probable that they involve first the formation of copper chlorides, by double decomposition between the copper sulphate and sodium chloride, and the subsequent action of these upon the silver sulphide present in the ore, thus—

$$2CuCl_2 + Ag_2S = 2AgCl + Cu_2Cl_2 + S.$$
$$Cu_2Cl_2 + Ag_2S = 2AgCl + Cu_2S.$$

The silver chloride dissolves in the sodium chloride present, and is reduced by the mercury, with the production of mercurous chloride (*calomel*), which is ultimately lost in the washing—

$$2AgCl + 2Hg = Hg_2Cl_2 + 2Ag.$$

The amalgam is first washed, and freed from adhering particles of mineral, and is then filtered through canvas bags, whereby the excess of mercury is removed. The solid residue, containing the silver, is then submitted to distillation.

In other amalgamation processes the ore is first roasted with salt, in order to convert the silver into chloride. The roasted ore is reduced to fine powder with water, and introduced into revolving casks along with scrap iron, when the chloride is reduced according to the equation—

$$2AgCl + Fe = 2Ag + FeCl_2,$$

and the reduced silver is then extracted by the addition of mercury, with which it amalgamates.

In the modern amalgamation process, the finely crushed ore, with water, is placed in iron pans provided with revolving machinery, which serves the purpose of further grinding, and also of mixing. When the ore is reduced to an almost impalpable powder, mercury is added, and the machinery is kept in operation for a few hours, when the amalgamation is complete; sometimes common salt and copper sulphate are added, either together or singly. Their presence does not appear to be necessary to the process, except in so far as they aid in keeping the surface of the mercury clean, or "quick;" for in the extremely finely divided condition to which the ore is reduced in this "pan" amalgamation process, the silver sulphide is readily acted upon by mercury, with the formation of mercuric sulphide—

$$Ag_2S + Hg = HgS + 2Ag,$$

and the silver so reduced, dissolves in the excess of mercury, from which it is finally separated by distillation.

(2.) **Processes by Means of Lead.**—When silver ores are smelted with lead, or with materials which yield metallic lead; in other words, when silver ores are smelted with lead ores, an alloy of silver and lead is obtained, from which the silver can be separated. When the argentiferous lead is rich in silver, the alloy is submitted to *cupellation*, which consists in heating the metal in a reverberatory furnace, the hearth of which consists of a movable, oval-shaped, shallow dish, made of bone ash, known as a *cupel*, or *test*. The alloy is fed into this cupel from a melting-pot, and a blast of air is projected upon the surface of the molten metal. The lead is thus converted into litharge, and the melted oxide, by the force of the blast, is made to overflow into iron pots. As the oxidation of the lead reaches completion, the thin film of litharge begins to exhibit iridescent interference colours, which presently disappear, leaving the brilliant surface of the melted silver. The sudden appearance of the bright metallic surface is known as the *flashing* of silver.

In the case of argentiferous lead too poor in silver to be directly cupelled, the alloy is submitted to one of two processes of concentration, namely, the *Pattinson process*, or the *Parkes's process*.

The *Pattinson process* for desilverising lead, depends upon the fact that alloys of silver and lead have a lower melting-point than ire lead, and therefore when argentiferous lead is melted and lowed to cool, the crystals which first form, consist of lead which nearly or quite pure, and the greater part of the silver is in ie still liquid portion. The operation is carried out in a row of on pots. A quantity of the metal is melted in one pot, and as cools, the crystals which begin to form are removed by means f a perforated iron ladle, and transferred to the next pot on ne side. This operation is continued until a definite proportion either two-thirds or seven-eighths, depending upon the proportion of silver) has been removed. The residue is then transferred the neighbouring pot on the opposite side, and a second charge ielted up in the first pot. As the neighbouring pots fill up, they re similarly treated, and in this way an alloy, gradually becoming cher and richer in silver, is passed along in one direction, and urer and purer lead is sent in the opposite way. The rich alloy then cupelled.

The *Parkes's process* depends upon the fact that when zinc is dded to a melted alloy of lead and silver, the zinc deprives the ad of the silver, and itself forms an alloy with it. The alloy of nc and silver rises to the surface, and is the first portion to solidify, nd can be removed. The operation is carried out in iron pots. he argentiferous lead is melted, and a quantity of zinc is oroughly stirred into the molten mass, the amount of zinc epending upon the richness of the lead. As the mixture cools, ie first portions to solidify are skimmed off with a ladle, and ansferred to another pot. These skimmings, consisting of zinc, lver, and lead, are first liquated ; that is, carefully heated to such temperature that the adhering lead melts, and flows away from ie less fusible zinc silver alloy. The solid alloy is then distilled, nd the residue, consisting of silver and lead, is submitted to upellation.

(3.) **Wet Processes** (*Ziervogel Process*).—When argentiferous yrites, or an artificially formed regulus containing sulphides of lver, copper, and iron, is roasted, the sulphides are first converted ito sulphates ; and, as the roasting continues, first the iron, then ie copper, and lastly, the silver sulphate is converted into oxide. y careful regulation, the process is continued until the whole f the iron and a part of the copper sulphates are decomposed. n lixiviating the roasted mass with water, the silver sulphate, ogether with the remaining copper sulphate, dissolves. From iis solution the silver is precipitated by scrap copper.

The copper is recovered from the solution by precipitation with iron.

*The Percy-Patera Process.*—In this method the ore is roasted with salt, and the silver chloride so formed is then extracted by means of sodium thiosulphate—

$$Na_2S_2O_3 + AgCl = NaCl + NaAgS_2O_3.$$

To the solution so obtained, sodium or calcium sulphide is added, which precipitates silver sulphide—

$$2NaAgS_2O_3 + Na_2S = Ag_2S + 2Na_2S_2O_3.$$

The silver sulphide is then reduced by being roasted in a reverberatory furnace.

**Properties.**—Silver is a lustrous white metal, which appears yellow when the light is reflected many times from its surface before reaching the eye. It is unacted upon by atmospheric oxygen, but quickly becomes tarnished by traces of sulphuretted hydrogen in the air. Silver has the highest conductivity for heat and electricity of all the metals. It is extremely malleable and ductile, being second only to gold. Thin films of silver appear blue by transmitted light. Silver melts at 954°, and, when heated by the oxyhydrogen flame, may be readily made to boil, and distil. The pure metal employed by Stas for the determination of the atomic weight, was obtained by distillation in this way. When volatilised in the electric arc, the vapour of silver has a brilliant green colour. Molten silver absorbs as much as twenty-two times its volume of oxygen, which it gives up again (with the exception of 0.7 volume) on solidification. As the mass cools, the oxygen evolved often bursts through the outer crust of solidified metal with considerable violence, ejecting portions of the still liquid silver as irregular excrescences, as seen in Fig. 136. This phenomenon is known as the "spitting" of silver. Small quantities of admixed metals prevent the absorption of oxygen.

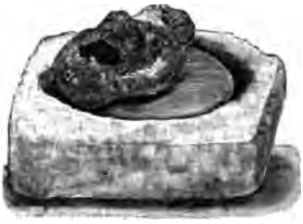

FIG. 136.

Silver is readily soluble in nitric acid, forming argentic nitrate, with liberation of oxides of nitrogen. Hot concentrated sulphuric acid converts it into argentic sulphate, with formation of sulphur dioxide (the reactions in both cases being the same as with copper).

**Silver Alloys.**—Silver, alloyed with copper, is largely employed for coinage, and for ornamental purposes. English *standard silver* contains 925 parts of silver per 1000. It is said, therefore, to have a *fineness* of 925. In France three standards are used. That for coinage contains 900 parts per 1000. For medals and plate the silver has a fineness of 950, while for jewellery it contains only 800 parts per 1000.

**Silver-plating.**—For purposes of electro-plating, a solution of silver cyanide in potassium cyanide is used. When a feeble electric current is passed through this solution (the article to be silvered being the negative electrode, and a plate of silver the positive), silver in a coherent form is precipitated upon the negative electrode, thereby coating the object; and cyanogen is disengaged at the positive pole, where it dissolves the electrode, reforming silver cyanide.

Silver is reduced from solutions, and deposited as a coherent film, by a variety of organic compounds; and various methods, based upon this property, are in use for obtaining mirrors, and silvered glass specula for optical purposes. One such method is the following. Two solutions are prepared, thus—

(1.) Ten grammes of silver nitrate are dissolved in a small quantity of water, and ammonia added until the precipitate dissolves. The liquid is then filtered, and diluted up to one litre.

(2.) Two grammes of silver nitrate are dissolved in a litre of boiling water, and 1.66 grammes of Rochelle salt (sodium potassium tartrate, $NaKC_4H_4O_6$) are added, and the liquid filtered. Equal volumes of these two solutions are poured into a shallow dish, and the glass to be silvered (after being perfectly cleaned) is laid in the solution. In about twenty minutes the silver will have formed a brilliant mirror upon the glass.*

**Oxides of Silver.**—Three oxides are believed to exist, namely—

| | |
|---|---|
| Silver monoxide . . . . | $Ag_2O$. |
| Silver peroxide . . . . | $Ag_2O_2$? |
| Silver suboxide . . . . | $Ag_4O$? |

**Silver Monoxide** (*argentic oxide*), $Ag_2O$, is obtained by adding sodium or potassium hydroxide to a solution of silver nitrate. A brown precipitate, consisting of hydrated oxide, is obtained, which when heated, is converted into the anhydrous compound. It is also formed when silver chloride is boiled with a strong solution of potassium hydroxide—

---

* By the reduction of silver solutions in the presence of certain organic compounds, Carey Lea has obtained the metal in the form of a dark bronze powder, which, when dry, resembles burnished gold. He has also obtained it exhibiting bluish-green and ruby-red colours. The material differs in many of its properties from ordinary silver, and is regarded by its discoverer as an allotropic form of silver (*American Journal of Science*, 1891).

$$2AgCl + 2KHO = 2KCl + H_2O + Ag_2O.$$

Silver oxide is a black amorphous powder, which when heated to 260°, begins to give off oxygen, and become reduced to metallic silver. It is a powerful oxidising substance, and when rubbed with sulphur, red phosphorus, sulphides of antimony or arsenic, or other readily oxidised substances, it causes them to ignite.

Silver oxide, although only very slightly soluble in water (1 part in about 3000), imparts to the solution a distinct metallic taste and an alkaline reaction.

It is reduced by hydrogen at 100°, with formation of water and metallic silver; and when brought into contact with peroxide of hydrogen, oxygen is evolved and metallic silver formed (see p. 203).

Silver oxide is soluble in strong ammonia, and, on standing, the solution deposits black shining crystals of the so-called *fulminating silver*. When dry, this compound is extremely explosive, and it often explodes when wet. Fulminating silver is believed to be the nitride, with the composition $NAg_3$.

**Silver Peroxide**, $Ag_2O_2$ (?).—When a solution of silver nitrate is submitted to electrolysis, a black powder, consisting of small octahedral crystals, is deposited upon the positive electrode. The same compound is obtained when a plate of silver is made the positive electrode in the electrolysis of acidulated water, and also when silver is acted upon by ozone. The exact composition of the compound has not been placed beyond doubt; it is believed to be a dioxide.

It readily parts with oxygen, and is a still more powerful oxidising agent than the monoxide. It dissolves in aqueous ammonia, with the evolution of nitrogen—

$$3Ag_2O_2 + 2NH_3 = 3Ag_2O + 3H_2O + N_2.$$

**Silver Suboxide**, $Ag_4O$ (?).—The black powder, obtained when silver citrate is reduced in a current of hydrogen at 100°, and potassium hydroxide is added to the aqueous solution of the residue, is believed to have the composition $Ag_4O$.

**Silver Chloride**, AgCl, is obtained as a white, bulky, curdy precipitate when a soluble chloride is added to silver nitrate. It melts at 451° to a yellowish liquid, which on cooling, congeals to a tough horny mass (hence the name *horn silver*, as applied to the native silver chloride). The precipitated chloride is soluble to a slight extent in strong hydrochloric acid, but readily soluble in alkaline chlorides, in ammonia, and in sodium thiosulphate. Potassium cyanide converts silver chloride into silver cyanide, which dissolves in the excess of alkaline cyanide, forming the double cyanide KCN,AgCN. When exposed to the light, silver chloride darkens in colour, assuming first a violet tint, and finally becoming dark brown or black (see Photo-salts, p. 522).

Silver chloride absorbs large volumes of ammonia, forming the compound $2AgCl,3NH_3$ (see p. 242).

**Silver Bromide,** AgBr, is prepared similarly to the chloride, the precipitated compound having a pale yellow colour. It is less soluble in ammonia than silver chloride; in dilute ammonia it is nearly insoluble. Silver bromide is decomposed by chlorine, and at a temperature of 100° by hydrochloric acid. At ordinary temperatures this reaction is reversed, hydrobromic acid converting silver chloride into the bromide.

Dry silver bromide does not absorb gaseous ammonia. Silver bromide is extremely sensitive to the action of light, and is the chief silver compound used in dry-plate photography.

**Silver Iodide,** AgI, may be obtained by precipitation from silver nitrate, with a soluble iodide; or by dissolving silver in strong hydriodic acid. As obtained by precipitation it is an amorphous yellow substance, less soluble in ammonia than either the bromide or chloride. It dissolves in hot hydriodic acid, which on cooling deposits colourless crystals of AgI,HI; the addition of water to the solution precipitates the normal iodide, AgI. Silver iodide absorbs gaseous ammonia, forming a white compound, $2AgI,NH_3$, which, on free exposure to the air, evolves ammonia, and is reconverted into the yellow iodide.

Silver iodide is the most stable of the three halogen compounds. When either the chloride or bromide is treated with hydriodic acid or potassium iodide, iodine replaces the other halogens, forming silver iodide.

**Silver Fluoride,** AgF.—This compound is markedly different in many respects from the other halogen silver salts. It is obtained by dissolving silver oxide or carbonate in hydrofluoric acid, and is deposited from the solution in colourless, quadratic pyramids, $AgF,H_2O$, or in prisms, $AgF,2H_2O$. The salt is extremely deliquescent, and very soluble in water. When dried in vacuo, the salt $AgF,H_2O$ undergoes partial decomposition, leaving a brownish residue. When heated, it is partially decomposed, according to the equation—

$$2AgF,H_2O = 2Ag + 2HF + H_2O + O.$$

The dry salt absorbs gaseous ammonia in large quantities, more than 800 times its own volume being taken up by the powdered substance.

**Silver Nitrate,** $AgNO_3$, is obtained by dissolving silver in nitric acid. It forms large colourless rhombic tables, which melt at 218°, and resolidify to a white, fibrous, crystalline mass, known as *lunar caustic*. Below a red heat it gives off oxygen, and forms silver nitrate; and at higher temperatures it is decomposed into metallic silver, and oxides of nitrogen. 100 parts of water at 0° dissolve 121.9 parts, and at 100°, 1110 parts of the crystallised salt; the solution is neutral. In contact with organic matter, silver nitrate is blackened on exposure to light. Thus, when the skin is touched with a solution of this salt, a few seconds' exposure to light causes a brown or black stain. Owing to this property, silver nitrate is employed for marking-inks. Silver nitrate absorbs gaseous ammonia, forming the compound $AgNO_3,3NH_3$, the absorption being accompanied with considerable rise of temperature. The compound $AgNO_3,2NH_3$ is deposited as rhombic prisms when aqueous silver nitrate is saturated with ammonia.

**Silver Sulphate,** $Ag_2SO_4$, is formed when silver, silver carbonate, or silver oxide is dissolved in sulphuric acid. It crystallises in rhombic prisms, isomorphous with sodium sulphate. With aluminium sulphate it forms an alum, in which the monovalent element silver, takes the place of potassium in common alum, $Ag_2SO_4,Al_2(SO_4)_3,24H_2O$.

**Photo-salts.**—This name has been applied by Carey Lea, to the coloured compounds formed by the action of light upon silver chloride, bromide, and iodide. The exact composition of the compounds that are formed when these silver salts are exposed to light is not definitely known. The change which they undergo has been attributed (1) to the partial reduction to metallic silver; (2) to the formation of sub-salts, such as $Ag_2Cl$, $Ag_2Br$, with elimination of chlorine or bromine; (3) to the formation of oxychloride or oxybromide; (4) to the production of double compounds of variable composition, of the sub-salt with the normal salt.

## GOLD.

Symbol, Au. Atomic weight = 196.8.

**Occurrence.**—This element occurs in nature almost exclusively in the uncombined condition, chiefly in quartz veins and in alluvial deposits formed by the disintegration of auriferous rocks. It is present in small quantities in many specimens of iron pyrites, copper pyrites, and many lead ores, from which it is often profitably extracted.

Gold is also met with in the form of an amalgam with mercury, and in combination with the element tellurium in the minerals *petzite* $(AgAu)_2Te$, and *sylvanite* $(AgAu)Te_2$.

**Extraction.**—Gold is extracted from auriferous quartz by causing the finely-crushed substance to flow, by means of a stream of water, over amalgamated copper plates. The gold particles adhere to the mercury, with which they amalgamate, and the amalgam so obtained is carefully removed and distilled.

From alluvial deposits, the native gold is separated by mechanical washing.

Gold is extracted from auriferous pyrites by means of chlorine. The ore is first carefully roasted, and, after being wetted, is exposed to the action of chlorine gas. The gold is thereby converted into the soluble auric chloride, $AuCl_3$, which is extracted by lixiviation, and precipitated by the addition of ferrous sulphate—

$$2AuCl_3 + 6FeSO_4 = 2Au + Fe_2Cl_6 + 2Fe_2(SO_4)_3.$$

Native gold usually contains silver, from which it may be separated by passing chlorine over the molten metal, in crucibles glazed with borax. The fused chloride of silver rises to the surface, and is prevented from volatilising by a covering of melted borax. When the operation is complete, the crucible is allowed to cool, when the gold solidifies, and the still liquid silver chloride is poured off.

**Properties.**—Gold is a soft yellow metal, which, when seen by light many times reflected from its surface, appears red. It is not acted upon by air or oxygen at any temperature, and does not decompose steam. No single acid is capable of attacking it (except selenic acid); but it is dissolved by aqua-regia, with formation of auric chloride. Gold is the most malleable and ductile of all the metals, and when beaten into very thin leaf, it appears green by transmitted light.

Gold is most easily reduced from its combinations. Most metals, when placed in a solution of a gold salt, precipitate the gold, and the most feeble reducing agents bring about the same result. On this account a solution of auric chloride is used for *toning* photographs. All the compounds of gold, when ignited in the air, are reduced to metallic gold. Gold is readily deposited upon other metals by the process of electro-gilding, the most suitable solution being that of the double cyanide of gold and potassium, $AuCN,KCN$.

**Gold Alloys.**—Alloys of gold with copper and with silver are used for coinage, and for ornamental purposes, pure gold being too soft for these purposes. Silver gives the alloy a paler colour than that of pure gold, while copper imparts to it a reddish tinge. The alloy used for English gold coin consists of gold, 11 parts; copper, 1 part. The proportion of gold in alloys is usually expressed in parts per 24 (instead of in percentages), these parts being termed *carats*. Thus pure gold is said to be 24-carat gold; 18-carat gold contains, therefore, 18 parts of gold and 6 parts of copper, or silver. Most countries have their own legal standards. In England the legal standard for gold coinage is 22-carats.

**Compounds of Gold.**—Gold forms two series of compounds, namely, *aurous*, in which the metal is monovalent, and *auric*, in which it is trivalent.

The composition of aurous compounds corresponds to that of the silver compounds. They are very readily decomposed. Thus, aurous chloride cannot exist in the presence of water, being decomposed into auric chloride and metallic gold. For this reason, when aurous oxide, $Au_2O$, is acted upon by aqueous hydrochloric acid, it forms auric, and not aurous chloride, thus—

$$3Au_2O + 6HCl = 2AuCl_3 + 3H_2O + 4Au.$$

With iodine, gold forms only aurous iodide, $AuI$; therefore, when auric oxide is acted upon by hydriodic acid, aurous iodide and free iodine are formed, thus—

$$Au_2O_3 + 6HI = 2AuI + 2I_2 + 3H_2O.$$

**Auric Chloride,** $AuCl_3$, is obtained by dissolving gold in aqua-regia, and evaporating the solution to dryness. When the residue is dissolved in water, the concentrated solution deposits reddish crystals of the composition $AuCl_3,2H_2O$. These lose their water when carefully heated, leaving a brown mass of deliquescent crystals. Auric chloride forms double chlorides with the alkaline chlorides, and with hydrochloric acid, which may be obtained as crystalline compounds. Thus, the compound $AuCl_3,HCl,3H_2O$ is deposited from a strong solution of gold in aqua-regia. This substance is sometimes termed *chloro-auric acid*, and the double compounds with metallic chlorides, such as $AuCl_3,NaCl,2H_2O$ and $(AuCl_3,KCl)_2H_2O$, are known as *chloro-aurates.*

**Auric Oxide**, $Au_2O_3$, is obtained as a brown powder, when the hydrated oxide, $Au_2O_3,3H_2O$ (or $Au(HO)_3$), is gently warmed. At 100° it begins to decompose, and at higher temperatures is completely converted into oxygen and metallic gold.

Auric oxide is feebly basic, forming a few unstable salts, in which gold replaces the hydrogen in acids. It is also a feeble acid-forming oxide, and forms salts called *aurates*, such as potassium aurate, $KAuO_2,3H_2O$, which may be regarded as being derived from an acid of the composition $HAuO_2$.

Auric oxide forms a compound with ammonia, known as *fulminating gold*, the exact composition of which is not known. It explodes with violence when dry, if struck, or gently warmed.

**Gold Sulphides.**—Two sulphides of gold have been obtained, aurous sulphide, $Au_2S$, and auro-auric sulphide, $Au_2S,Au_2S_3$ (or AuS). The latter is formed when sulphuretted hydrogen is passed into a cold solution of auric chloride—

$$8AuCl_3 + 9H_2S + 4H_2O = 2(Au_2S,Au_2S_3) + 24HCl + H_2SO_4.$$

# CHAPTER VI

## *ELEMENTS OF GROUP II. (FAMILY A.)*

| | Atomic Weights. | | Atomic Weights. |
|---|---|---|---|
| *Beryllium*, Be | 9.08 | Strontium, Sr | 87.3 |
| Magnesium, Mg | 23.94 | Barium, Ba | 136.86 |
| Calcium, Ca | 39.91 | | |

WITH the exception of the rare element beryllium, these metals were first obtained (although not in the pure state) by Davy, who, soon after his discovery of the metals potassium and sodium, showed that the so-called *earths* were not elementary bodies as had been supposed, but were compounds of different metals with oxygen.

The element beryllium is of later discovery, for although as early as 1798 it had been shown by Vanquelin that the particular "earth" in the mineral *beryl* was different from any other known earth, it was not until 1827 that the metal it contained was isolated by Whöler. In a state approaching to purity, beryllium was first prepared by Humpidge, 1885.

None of the elements of this family occurs in nature in the uncombined condition; and, with the exception of magnesium, the metals themselves, in their isolated condition, are at present little more than chemical curiosities. In the case of beryllium this is due to the comparative rarity of its compounds; but with calcium, strontium, and barium, whose compounds are extremely abundant, it is owing partly to the difficulty of isolating the metals in a pure state, and also to the fact that hitherto they have received no useful application. Beryllium and magnesium are white metals, which retain their lustre in the air. Calcium, strontium, and barium have a yellow colour, and on exposure to air become converted into oxide.

All these metals form an oxide of the type RO. Beryllium oxide is insoluble in water; magnesium oxide is very slightly soluble (1 part in 55,000 or 100,000 parts of water), but the solution shows a feeble alkaline reaction. The calcium, strontium, and barium oxides show increasing solubility, and stronger alkalinity and causticity. On this account these elements are known as the *metals of the alkaline earths.* These three elements also form peroxides of the type $RO_2$.

All the monoxides are basic, and combine with acids to form salts of the types $RCl_2$, $RSO_4$, $R(NO_3)_2$.

The element beryllium (the typical element) stands apart from the others of this family in many of its chemical relations. Thus, the oxide BeO, unlike the corresponding compounds of the other elements, does not combine with water to form the hydroxide. The hydroxide $Be(HO)_2$ is soluble in sodium and potassium hydroxide. In this respect beryllium exhibits its resemblance to zinc. The chloride also differs from the other chlorides in being volatile.

In its permanence in air, its colour, its high melting-point, the solubility of its sulphate, and the readiness with which its hydroxide is converted by heat into the oxide, beryllium exhibits a close similarity to magnesium. In the solubility of its hydroxide in potassium hydroxide, and in its inability to decompose water, beryllium also shows a marked resemblance to zinc.

The three elements, calcium, strontium, and barium, exhibit a closer resemblance to each other in most of the physical and chemical relations, than to either magnesium or beryllium.

They are readily distinguished by their different spectra. Barium salts, when heated in a non-luminous flame, impart to it a green colour. Calcium and strontium, under the same circumstances, each give a red colour; but the red imparted by strontium compounds is more brilliant, and less orange, than that of calcium salts. When the flames are examined by the spectroscope, the most characteristic lines given by barium, are two in the bright green (Ba$\alpha$ and Ba$\beta$). These are accompanied by a number of less brilliant lines. The spectrum of strontium consists of four specially prominent lines, one in the bright blue (Sr$\delta$), one in the orange (Sr$\alpha$), and two in the red (Sr$\beta$ and Sr$\gamma$), with others less pronounced; while that of calcium contains one brilliant green line (Ca$\beta$), and one equally brilliant orange line (Ca$\alpha$), besides a large number of less prominent lines.

## BERYLLIUM.

Symbol, Be. Atomic weight = 9.08.

**Occurrence.**—This element occurs principally in the mineral *beryl*, a double silicate of the composition $3BeO,Al_2O_3,6SiO_2$. The transparent varieties are used as gems, the transparent green beryl being the precious *emerald*.

*Phenacite* is beryllium silicate, $Be_2SiO_4$, while *chrysoberyl* has the composition $BeO,Al_2O_3$.

**Formation.**—The element is obtained by heating sodium in the vapour of beryllium chloride, all air having been previously replaced by hydrogen. The product is afterwards melted beneath fused sodium chloride, when it is obtained as a coherent of solid metal.

**Properties.**—Beryllium is a white metal resembling magnesium. It has a specific gravity of 2.1, and is moderately malleable. It does not readily tarnish in the air at ordinary temperatures, but, when strongly heated, becomes coated with a protecting film of oxide. The powdered metal, when heated, takes fire, and burns with a bright light. It has no action upon water, even at the boiling temperature.

Beryllium is easily dissolved by dilute hydrochloric acid, with evolution of hydrogen. Cold dilute sulphuric acid is without action, but, when heated, slowly dissolves it. Nitric acid slowly attacks it when concentrated and hot. It readily dissolves in potassium hydroxide, with evolution of hydrogen.

**Beryllium Compounds.**—The best known are the oxide (*berylla*), BeO, a white infusible powder, insoluble in water, soluble in acids; the chloride, $BeCl_2$, obtained by heating the oxide with charcoal in a stream of chlorine, a white crystalline solid, readily fused and volatilised.

Beryllium compounds do not impart any colour to a Bunsen flame. They are characterised by possessing a sweet taste, hence the name of *glucinum* originally given to this element.

## MAGNESIUM.

Symbol, Mg. Atomic weight = 23.94.

**Occurrence.**—Magnesium is not found in the uncombined state. In combination it is widely distributed, and is extremely abundant. In the mineral *dolomite*, associated with lime as carbonate, it occurs in mountainous masses.

*Magnesite*, $MgCO_3$; *kieserite*, $MgSO_4,H_2O$; *carnallite*, $MgCl_2,KCl,6H_2O$, are amongst the commoner naturally occurring magnesium compounds. It is also a constituent of *asbestos*, *meerschaum*, *serpentine*, *talc*, and a large number of other silicates. As sulphate and chloride it is met with in sea water and many saline springs.

**Modes of Formation.**—Magnesium can be obtained by the sis of the fused chloride, or a mixture of magnesium and m chlorides.

larger scale magnesium is prepared by reducing the chloride lium. A mixture of anhydrous magnesium chloride (or ixed chlorides of magnesium and sodium, or potassium), d cryolite, and sodium is thrown into a red-hot crucible, quickly closed. A violent reaction takes place, at the on of which the melted mixture is stirred with an iron rod the globules of magnesium to run together.

rude metal is afterwards purified by distillation.

**rties.**—Magnesium is a silvery-white metal, which does ish in dry air, but becomes coated with a film of oxide posed to air and moisture. At a red heat it melts, and at temperatures may be distilled. When heated in the air it e, and burns with a dazzling white light, which is extremely he chemically active rays. The flash of light, obtained by g a small quantity of magnesium filings into a spirit flame, for photographic purposes. Magnesium is only moderately le, and is only ductile at high temperatures; it is readily into the form of wire at a temperature slightly below its point. Magnesium does not decompose water even at the point; but when strongly heated in a current of steam, the kes fire (p. 152). Magnesium is rapidly dissolved by dilute ith brisk evolution of hydrogen, but solutions of caustic are unacted upon it (compare Zinc). When heated with solutions of ammonium salts, hydrogen is evolved, and a salt of magnesium and ammonium is found in the solution. esium combines directly with nitrogen, when strongly n that gas, forming magnesium nitride, $N_2Mg_3$ (p. 208). count of the brilliant light emitted by burning magnesium, ployed for signalling purposes, and also in pyrotechny.

**esium Oxide** (*magnesia*), MgO, is found native as the *periclase*. It is formed when magnesium burns in the air, magnesium carbonate is submitted to prolonged gentle ion, when it is obtained as a white, bulky powder, known in ce as *calcined magnesia* or *magnesia usta*.

esia is extensively manufactured from the magnesium occurring in the Stassfurt deposits, by first converting the into carbonate, and subjecting this to calcination. Mag- s been obtained in the crystalline form, identical with that lase, by heating the amorphous compound in a stream of gaseous hydrochloric acid. It may be fused in the oxyhydrogen flame, and on cooling, it solidifies to a vitreous mass which is sufficiently hard to cut glass. On account of its extreme refractoriness, magnesia is used for a variety of metallurgical purposes, such as the manufacture of crucibles, cupels, &c.

**Magnesium Hydroxide,** $Mg(HO)_2$, is found in nature as the mineral *brucite.* It is prepared by precipitating a magnesium salt by sodium or potassium hydroxide. At a dull red heat it loses water, and is converted into the oxide, and the magnesia so obtained has the property of rehydrating itself in contact with water, with evolution of heat.

Magnesium hydroxide slowly absorbs carbon dioxide, forming the carbonate; owing to this fact, and to the property it possesses of rehydration, magnesia that has been prepared by calcination at a low temperature can be employed as a cement. Thus, if calcined magnesite be made into a paste with water, the mixture is found to harden in about twelve hours, and ultimately to acquire a hardness equal to that of Portland cement.

**Magnesium Chloride,** $MgCl_2$.—This salt is formed when magnesia, or magnesium carbonate, or the metal itself, is dissolved in hydrochloric acid. From this solution monosymmetric crystals of the composition $MgCl_2 \cdot 6H_2O$ are deposited. When this salt is heated it loses water, and at the same time is partially decomposed [illegible] and magnesia; in order, therefore, to pre[illegible] the double magnesium ammo[illegible] ammonium chloride to a [illegible] evaporation the double salt [illegible] This salt allows itself to be [illegible] decomposition of the magne[illegible] strongly heated. [illegible] magnesium [illegible] a white crystalline [illegible] and dissolves in water [illegible] forms double [illegible] The potassium [illegible] as the mineral [illegible] of magnesium [illegible] magnesia the [illegible] and is found [illegible] $MgCl_2 \cdot MgO$, associated with varying quantities of water. The white deposit which forms in bottles containing the solution known as *magnesia mixture*, consists of $MgCl_2,5MgO,13H_2O$.

When magnesium oxychloride is heated to redness in a current of air, the magnesium is converted into oxide, and a mixture of chlorine and hydrochloric acid is evolved. The reaction may be represented as taking place as follows—

$$2MgCl_2 + H_2O + O = 2MgO + 2HCl + Cl_2.$$

The Weldon-Pechiney process for manufacturing chlorine is based upon this reaction.

**Magnesium Sulphate**, $MgSO_4$ (*Epsom salts*), is met with in many mineral springs, and in large quantities as the mineral *kieserite*, $MgSO_4,H_2O$.

Magnesium sulphate may be obtained by decomposing *dolomite*, $(CaMg)CO_3$, with sulphuric acid, the nearly insoluble calcium sulphate being readily removed from the soluble magnesium salt. Magnesium sulphate is now very largely manufactured from *kieserite*, which in contact with water is converted from the slightly soluble monohydrated salt, into $MgSO_4,7H_2O$, which is readily soluble, and is purified by recrystallisation. As usually obtained, crystallised magnesium sulphate, $MgSO_4,7H_2O$, forms colourless rhombic prisms; but when deposited from a cold supersaturated solution, it sometimes forms prisms belonging to the monosymmetric (monoclinic) system, having the same degree of hydration. Above 50°, monosymmetric prisms of the composition $MgSO_4,6H_2O$ are deposited.

When the ordinary salt, $MgSO_4,7H_2O$, is placed over sulphuric acid, it loses two molecules of water: when heated to 150° it loses six molecules, and at 200° it becomes anhydrous. At the ordinary temperature, 100 parts of water dissolve 126 parts of crystallised magnesium sulphate; the solution has a bitter taste, and acts as a purgative. With alkaline sulphates, magnesium sulphate forms a series of double salts, having the general formula $MgSO_4,R_2SO_4,6H_2O$. They are isomorphous with each other, crystallising in monosymmetric prisms. The potassium salt occurs in the Stassfurt deposits as *schönite*.

When anhydrous magnesium sulphate is dissolved in hot sulphuric acid, two acid sulphates are obtained. One, having the composition $MgSO_4,H_2SO_4$, is deposited from the hot solution; while from the cold liquid the salt that crystallises has the composition $MgSO_4,3H_2SO_4$. They are at once decomposed by water.

**Magnesium Carbonate,** $MgCO_3$, occurs as the mineral *magnesite*, which is sometimes found as rhombohedral crystals, isomorphous with crystals of *calcite* ($CaCO_3$). Magnesium exhibits a great tendency to form basic and hydrated carbonates; the normal carbonate, $MgCO_3$, is therefore not obtained by precipitating a magnesium salt with an alkaline carbonate; the white precipitate formed under these circumstances is a basic carbonate, whose composition varies with the conditions of precipitation. If, however, this precipitate be suspended in water, and the liquid saturated with carbon dioxide, the compound dissolves (more readily under increased pressure), and when the solution is heated to 300° under pressure, in such a manner that the evolved carbon dioxide can escape, the normal anhydrous carbonate is deposited in rhombohedral crystals isomorphous with calcite. If the solution be evaporated to dryness, the normal carbonate is deposited in rhombic crystals isomorphous with *arragonite* ($CaCO_3$). Magnesium and calcium carbonates are therefore isodimorphous.

**Basic Carbonates.**—The mineral *hydromagnesite* is a basic carbonate of the composition $3MgCO_3,Mg(HO)_2,3H_2O$. A number of basic carbonates are formed by the precipitation of a magnesium salt with sodium carbonate. Thus, under ordinary conditions a white bulky precipitate is obtained, known in pharmacy as *magnesia alba levis*. Its composition, although liable to vary through the presence of other basic carbonates, is in the main the same as that of hydromagnesite.

If the precipitation be made with boiling solutions, and the precipitate so obtained be dried at 100°, a denser carbonate is obtained, termed *magnesia alba ponderosa*, $4MgCO_3,Mg(HO)_2,4H_2O$.

When an excess of sodium carbonate is employed, and the mixture is subjected to prolonged boiling, a carbonate is obtained, having the composition $2MgCO_3,Mg(HO)_2,2H_2O$.

## CALCIUM.

Symbol, Ca. Atomic weight = 39.91.

**Occurrence.**—Calcium is only met with in nature in combination. It occurs in enormous quantities as the carbonate, in a great variety of different minerals, such as *marble*, *limestone*, *calcspar*, and also as *coral*; and with carbonate of magnesia as *dolomite*, or *magnesian limestone.* In combination with sulphuric acid, calcium occurs as *gypsum* and *selenite*, $CaSO_4,2H_2O$, and as *anhydrite*, $CaSO_4$. The fluoride $CaF_2$ occurs as *fluorspar;* and the various silicious rocks contain compound silicates of calcium and other metals. The carbonate and sulphate are present in most spring and river waters. Calcium compounds are also present in all vegetable and animal organisms. Thus, bones consist largely of calcium phosphate.

**Modes of Formation.**—Although calcium compounds are so extremely abundant, the element itself is a rare substance. The element was first isolated in an impure state by Davy (1808). It may be obtained by the electrolysis of the fused chloride, or by fusing together calcium chloride, sodium, and zinc, when an alloy of zinc and calcium is obtained, from which the zinc is removed by distillation.

**Properties.**—Calcium is a yellow metal, somewhat the colour of pale brass. It is sufficiently hard to be worked with a file, and may be hammered out into leaf. In moist air it is soon converted into the hydroxide, but in dry air it remains untarnished for a considerable time. It decomposes water at the ordinary temperature, with rapid evolution of hydrogen. When heated in the air, it takes fire and burns.

**Oxides of Calcium.**—Two oxides are known, namely, calcium monoxide, CaO, and calcium dioxide, $CaO_2$.

**Calcium Oxide** (*lime, quicklime*), CaO, is obtained by heating calcium carbonate to redness—

$$CaCO_3 = CO_2 + CaO.$$

On a large scale, lime is manufactured by burning limestone or chalk in kilns with coal. If much clay be present with the limestone, care is required to prevent the mass from fusing, when it is said to be *dead burnt.* Lime is a white amorphous substance, which is infusible by the oxyhydrogen flame ; but which, when so heated, emits a bright light, known as the oxyhydrogen lime-light. It absorbs moisture and carbon dioxide from the air. On account of its power of absorbing moisture, lime is frequently employed as a dehydrating agent. Thus, gases which cannot be dried by means of sulphuric acid (*e.g.*, ammonia) may be deprived of moisture by being passed over calcium oxide. It is also used for withdrawing water from alcohol, in the preparation of absolute alcohol. When a small quantity of water is poured upon lime, the mass rapidly becomes hot, and volumes of steam are given off; the lime at the same time swelling up and crumbling to a soft, dry powder. This process is known as the *slaking* of lime, and the product is termed *slaked lime*, in contradistinction to *quick lime*. The lime enters into chemical union with water, forming calcium hydroxide, thus—

$$CaO + H_2O = Ca(HO)_2.$$

**Calcium Hydroxide,** $Ca(HO)_2$, is a white amorphous powder, sparingly soluble in water; and, unlike the majority of solids, it is less soluble in hot than in cold water. One hundred parts of water at the ordinary temperature dissolve 0.14 parts of calcium hydroxide, while at 100° the same volume of water dissolves about half that amount. This solution, known as *lime water*, has an alkaline reaction, and absorbs carbon dioxide, with the precipitation of calcium carbonate.

**Milk of Lime** is the name given to a mixture of lime with less water than will dissolve it, whereby an emulsion of lime is obtained. When a thick paste of lime and water is exposed to the atmosphere, in a few days it sets, and continues gradually to harden. On this account lime is used for mortars and cements. Mortar consists of a mixture of lime and sand with water. The sand serves the double purpose of preventing shrinkage on drying, and also of rendering the mass more permeable to atmospheric carbon dioxide. The setting of mortar is due to the combined action of evaporation and absorption of carbon dioxide.

**Calcium Dioxide,** $CaO_2$, is obtained by adding lime-water to hydrogen peroxide, or to sodium peroxide acidulated with dilute nitric acid: sparingly soluble crystals of $CaO_2,8H_2O$ separate out, which at 130° lose their water. When more strongly heated, the monoxide is formed, with evolution of oxygen.

**Calcium Chloride,** $CaCl_2$, occurs in sea and river waters, and is present in *carnallite* and *tachydrite*, of the Stassfurt deposits. It is obtained in large quantities as a bye-product in many manufacturing processes, such as that of potassium chlorate, ammonia from ammonium chloride, &c. It may be obtained by the action of hydrochloric acid upon calcium carbonate, and is deposited on concentration, in large colourless, deliquescent, hexagonal prisms, $CaCl_2,6H_2O$, which melt at 29° in their water of crystallisation. When heated below 200°, the crystals part with four molecules of water, and above 200° become anhydrous. As thus obtained, the anhydrous salt is a porous mass, which is extremely hygroscopic, and on this account is used as a desiccating agent, both for gases and liquids. At a red heat it fuses, and on cooling, solidifies to a crystalline, deliquescent mass. Calcium chloride combines with ammonia, forming the compound $CaCl_2 8NH_3$. Calcium chloride, therefore, cannot be employed for drying gaseous ammonia.

Crystallised calcium chloride is extremely soluble in water; 100 parts of water at 16° dissolve 400 parts of the salt, the solution being attended with considerable absorption of heat. When mixed with powdered ice, or snow, liquefaction of both the solids rapidly takes place (owing to the formation of a cryohydrate), and the consequent absorption of heat, lowers the temperature of the mixture to $-40°$.

**Bleaching-Powder** (*chloride of lime*), $Ca(OCl)Cl$.—This important compound is manufactured on a large scale by the action of chlorine upon slaked lime. The hydrated lime is spread upon the floor of the bleaching-powder chambers to a depth of three or four inches, and raked into ridges or furrows with a special wooden rake. Chlorine is then led into the chambers, which are provided with glass windows to enable the operator to examine the colour of the atmosphere within. At first the absorption of the chlorine is rapid, but as the reaction proceeds it becomes slower, and the lime is from time to time raked over to expose a fresh surface. The lime is left in contact with the gas for twelve to twenty-four hours. The excess of chlorine is absorbed by projecting into the chamber a shower of fine lime-dust, by means of a mechanical fan-distributor. This, in settling, rapidly absorbs all the chlorine, and the chambers can then be opened without any unpleasant smell of chlorine being perceptible.

The reaction which takes place is expressed by the equation—

$$Ca(HO)_2 + Cl_2 = Ca(OCl)Cl + H_2O.$$

It was formerly believed that bleaching-powder was a mechanical mixture of calcium chloride, $CaCl_2$, and calcium hypochlorite, $Ca(OCl)_2$, but it has been conclusively shown that the substance does not contain any free calcium chloride. It may, however, be regarded as a compound consisting of equivalent proportions of these two salts, and its composition may be expressed by the formula $Ca(OCl)_2, CaCl_2$, which corresponds to $2Ca(OCl)Cl$.

The relation in which bleaching-powder stands to calcium chloride on the one hand, and calcium hypochlorite on the other, will be seen by the following formulæ—

| Calcium Chloride. | Calcium Hypochlorite. | Bleaching-Powder, or Calcium Chloro-hypochlorite. |
|---|---|---|
| Cl—Ca—Cl | ClO—Ca—OCl | Cl—Ca—OCl. |

In practice, the absorption of chlorine by the lime is never as complete as is represented by the above equation, and the commercial value of the product depends upon the amount of *available chlorine* it contains, *i.e.*, chlorine which is evolved on treating the compound with hydrochloric or sulphuric acid. This ranges from 30 to 38 per cent.

When treated with water, bleaching-powder is converted into calcium chloride and hypochlorite, thus—

$$2Ca(OCl)Cl = CaCl_2 + Ca(OCl)_2.$$

Bleaching-powder decomposes slowly even in stoppered bottles, and more rapidly on exposure to atmospheric moisture and carbon dioxide.

When acted upon by acids, chlorine is evolved, thus—

$$Ca(OCl)Cl + 2HCl = CaCl_2 + H_2O + Cl_2$$
$$Ca(OCl)Cl + H_2SO_4 = CaSO_4 + H_2O + Cl_2.$$

When a solution of bleaching-powder is treated with very dilute acids, hypochlorous acid is first liberated, which in contact with hydrochloric acid yields chlorine—

$$(1)\quad Ca(OCl)_2.Aq + 2HCl.Aq = CaCl_2 + 2HClO.Aq.$$
$$(2)\quad HClO + HCl = H_2O + Cl_2.$$

In the process of bleaching, the material is first steeped in a dilute solution of bleaching-powder, and then in dilute acid. The hypochlorous acid first formed is decomposed in the presence of excess of hydrochloric acid, generating chlorine within the fibres of the wet cloth.

**Calcium Sulphate,** $CaSO_4$, occurs as the mineral *anhydrite*, and in the hydrated condition as *gypsum*, $CaSO_4,2H_2O$, of which *satinspar* (or *fibrous gypsum*), *alabaster*, and *selenite* are different varieties. It is obtained in the hydrated condition by precipitation from a solution of calcium chloride, on the addition of sulphuric acid or a soluble sulphate. When dried at 110° to 120° it loses a portion of its water, leaving the hydrate, $(CaSO_4)_2,H_2O$ ; at 200° it becomes anhydrous. Calcium sulphate, in the hydrated condition, is slightly soluble in water, the solubility reaching a maximum at 35°, when 1 part of the compound requires 432 parts of water for its solution; above this temperature the solubility again diminishes. Its solubility is increased by the presence of alkaline chlorides and free hydrochloric acid.

When boiled in strong sulphuric acid, calcium sulphate partially dissolves, and on cooling, an acid sulphate crystallises out, having the composition $CaSO_4,H_2SO_4$.

**Plaster of Paris** is calcium sulphate which has been partially deprived of its water of hydration by heat, and converted into the hydrate, $(CaSO_4)_2H_2O$. It is manufactured by burning gypsum in a kiln, or oven, in such a way that the carbonaceous fuel does not come in contact with the sulphate, which would result in its reduction to sulphide; the temperature is not allowed to exceed about 130°. If heated more strongly (above 200°) the sulphate becomes anhydrous, and is said to be *dead burnt;* in this condition its property of *setting* when mixed with water is greatly impaired. When plaster of Paris is made into a paste with water, it rapidly sets to a hard mass: this setting is due to its rehydration, whereby gypsum is reformed, thus—

$$(CaSO_4)_2,H_2O + 3H_2O = 2CaSO_4,2H_2O.$$

**Calcium Carbonate,** $CaCO_3$.—This compound is extensively met with in nature, as *limestone*, *chalk*, *marble*, and innumerable varieties of *calcspar*. It is formed when lime is exposed to atmospheric carbon dioxide. It is obtained when an alkaline carbonate is added to a soluble calcium salt.

Calcium carbonate is dimorphous; it occurs as *arragonite* in crystals belonging to the rhombic system, and as calcspar in crystals belonging to the hexagonal system. Both these crystalline varieties can be artificially obtained: when deposited from solutions at the ordinary temperature, the crystals are identical with calcite; but when crystallised from hot solutions, they form rhombic crystals corresponding to arragonite.

Calcium carbonate is nearly insoluble in water; 1000 grammes of water dissolve .0018 grammes of the compound. It is more soluble in water charged with carbon dioxide, forming the acid carbonate of lime, $CaCO_3,H_2CO_3$, or $H_2Ca(CO_3)_2$.

1000 grammes of water saturated with carbon dioxide will dissolve, at 0°, 0.7 grammes of calcium carbonate. By increasing the pressure (thereby increasing the amount of dissolved gas) as much as 3 grammes of calcium carbonate may be dissolved. When this solution is boiled, the acid carbonate is decomposed (p. 197).

**Calcium Phosphate** (*tricalcium orthophosphate*), $Ca_3(PO_4)_2$, is the most important of the phosphates of calcium. It is found as the mineral *osteolite*, $Ca_3(PO_4)_2,2H_2O$, and also as *sombrerite*, *estramadurite*, and *coprolites*. *Apatite* consists of phosphate and fluoride, $3Ca_3(PO_4)_2,CaF_2$; and the mineral constituents of bones consist chiefly of calcium phosphate.

It is obtained in a pure state by the addition of ordinary sodium phosphate to a solution of calcium chloride, in the presence of ammonia. The precipitate is decomposed on boiling, into an insoluble basic salt, and a soluble acid salt. Although nearly insoluble in pure water, calcium phosphate dissolves in water containing salts in solution, such as sodium chloride or nitrate, or even dissolved carbon dioxide. On this fact depends the readiness with which this substance is absorbed by the roots of plants.

Calcium phosphate is readily soluble in both nitric and hydrochloric acids. It is decomposed by sulphuric acid, with the formation of monocalcium orthophosphate and calcium sulphate, thus—

$$Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + H_4Ca(PO_4)_2.$$

This mixture of calcium sulphate and monocalcium phosphate is known as *superphosphate of lime*, and is largely used as an artificial manure.

With a larger quantity of sulphuric acid, the phosphate is converted into tribasic phosphoric acid. (See Phosphorus, p. 414.)

**Calcium Sulphide**, CaS, is formed when sulphuretted hydrogen is passed over heated lime—

$$Ca(HO)_2 + H_2S = CaS + 2H_2O.$$

Or by heating calcium sulphate with carbon—

$$CaSO_4 + 4C = CaS + 4CO.$$

Calcium sulphide is decomposed on boiling with water, forming calcium hydroxide and hydrosulphide, thus—

$$2CaS + 2H_2O = Ca(HO)_2 + Ca(HS)_2.$$

Calcium sulphide (in common with barium and strontium sulphides), *as usually obtained*, possesses the property of emitting a feeble light (or phosphorescence) in the dark, after being previously exposed to a bright light. The light emitted gradually diminishes in intensity, but on re-exposing the compound to the light, its luminosity is again restored. This property has been long known, and calcium sulphide was formerly termed *Canton's phosphorus.* The material formerly known as *Bononian* (or *Bolognian*) *phosphorus* is the corresponding barium compound.

These various sulphides are now manufactured for the preparation of so-called luminous paint. The phosphorescence of these compounds appears to be due to the presence of small quantities of foreign substances; thus, not only is the particular colour of the light emitted changed by the intentional introduction of minute traces of bismuth, cadmium, manganese, zinc, and many other metals, but it has been shown, in the case of calcium sulphide, that the perfectly pure substance does not exhibit phosphorescence.

## STRONTIUM.

Formula, Sr. Atomic weight = 87.3.

**Occurrence.**—The chief natural compounds of this element are *strontianite*, $SrCO_3$, and *celestine*, $SrSO_4$.

**Modes of Formation.**—The metal was first obtained in small quantity by Davy, by the electrolysis of the hydroxide, or chloride, moistened with water.

It is more advantageously obtained by electrolysing the fused chloride. An amalgam of mercury and strontium (from which the strontium may be separated by volatilising the mercury in a stream of hydrogen) has been obtained by heating a saturated solution of strontium chloride with sodium amalgam.

**Properties.**—Strontium is a yellowish metal resembling calcium. It is readily oxidised by air, and decomposes water at ordinary temperatures; when heated in the air it burns brilliantly.

**Oxides of Strontium.**—Two oxides, corresponding to those of calcium, are known, namely, strontium monoxide, SrO, and dioxide, $SrO_2$.

**Strontium Monoxide** (*strontia*), SrO, is obtained by heating the nitrate or carbonate. It is prepared on a large scale by decomposing strontium carbonate by superheated steam ; carbon dioxide is evolved, and strontium hydroxide remains, which on ignition forms the monoxide. Strontia strongly resembles lime. When treated with water it slakes with evolution of heat, forming strontium hydroxide, $Sr(HO)_2$. The hydroxide is more soluble in water than the lime compound, and the solution on cooling deposits quadratic crystals, $Sr(HO)_2,8H_2O$. The solution is strongly alkaline.

Strontium hydroxide combines with sugar, forming a saccharate of strontia, which is readily decomposed by carbon dioxide. On this account it is prepared on a large scale for use in the manufacture of beet-sugar. One process by which it is obtained on a commercial scale, consists in first forming strontium sulphide, by reducing the natural sulphate with carbon, and treating the solution of the sulphide with sodium hydroxide, thus—

$$SrS + NaHO + H_2O = Sr(HO)_2 + NaHS.$$

**Strontium Dioxide,** $SrO_2$.—When hydrogen peroxide is added to a solution of strontium hydroxide, a hydrate of the peroxide separates out in the form of pearly crystals, $SrO_2,8H_2O$. On gently heating this compound, it is converted into the anhydrous peroxide. On heating to redness it evolves oxygen, and is converted into the monoxide.

**Strontium Chloride,** $SrCl_2$, is obtained from strontianite by the action of hydrochloric acid. The salt deposits from the solution in deliquescent hexagonal prisms, $SrCl_2,6H_2O$, isomorphous with the corresponding calcium compound.

**Strontium Sulphate,** $SrSO_4$.—The native compound *celestine* occurs in amorphous fibrous masses, and also in rhombic crystals. The name of the mineral is derived from the fact that it usually has a light-blue colour. It is produced by precipitation from a strontium salt by sulphuric acid. It is only slightly soluble in cold water, and still less in hot. When boiled with solutions of alkaline carbonates, strontium sulphate is completely converted into strontium carbonate—

$$SrSO_4 + Na_2CO_3 = SrCO_3 + Na_2SO_4.$$

In this respect strontium sulphate differs from barium sulphate, which under these conditions remains unchanged. On treatment with strong sulphuric acid, strontium sulphate forms $SrSO_4,H_2SO_4$, which, like the corresponding calcium compound, is converted by water into sulphuric acid and the normal sulphate.

**Strontium Nitrate,** $Sr(NO_3)_2$, is obtained by dissolving the natural carbonate in dilute nitric acid. On concentration, the anhydrous salt separates out in regular octahedrons. From dilute solution, on cooling, it forms monosymmetric prisms, $Sr(NO_3)_2$, $4H_2O$, which effloresce on exposure to the air. When heated with carbon, or other readily combustible substances, the mixture inflames, and burns with the red colour characteristic of strontium compounds; strontium nitrate is therefore largely used in pyrotechny for the production of red fire. This property is most readily illustrated by mixing dry powdered strontium nitrate with ammonium picrate, and igniting the mixture, which burns with a brilliant red light.

## BARIUM.

Symbol, Ba. Atomic weight = 136.86.

**Occurrence.**—The most abundant natural compounds of barium are *heavy spar*, $BaSO_4$, and *witherite*, $BaCO_3$. It occurs also, associated with calcium, in the mineral *barytocalcite*, $BaCO_3,CaCO_3$.

**Modes of Formation.**—The element barium is more difficult to isolate than either strontium or calcium, and it is doubtful whether pure barium has ever been obtained. Davy electrolysed various barium salts, made into a thick paste with water, using mercury as the negative electrode: in this way an amalgam of barium was formed, from which, on distilling away the mercury, a dark porous mass was obtained. Amalgams of barium and mercury have been prepared in other ways, but it has been shown that the product obtained after distilling the mercury from these, is not pure barium, but is a solid alloy or compound of barium with mercury.

By the electrolysis of the fused chloride, Matthiessen obtained small globules of metal, which on exposure to the air rapidly oxidised. More recent experimenters fail to obtain the metal by this process (Limb., *compt. rend.*, 112).

**Oxides of Barium.**—Two oxides are known, namely, barium monoxide, BaO, and dioxide, $BaO_2$.

**Barium Monoxide** (*baryta*), BaO, is usually prepared by heating the nitrate. The mass fuses and evolves oxygen and oxides of nitrogen, leaving a greyish white friable residue of the oxide. It may also be obtained by heating the carbonate; but as the temperature necessary to expel the carbon dioxide is very high, it is usual to mix the carbonate with lampblack, tar, or other substances which on heating will yield carbon, when the conversion takes place more readily, carbon monoxide being evolved, thus—

$$BaCO_3 + C = BaO + 2CO.$$

Small quantities may readily be obtained by heating barium iodate in a porcelain crucible, when the iodate is decomposed as follows—

$$Ba(IO_3)_2 = BaO + I_2 + 5O.$$

Barium oxide is a strongly caustic and alkaline compound; in contact with water it slakes with evolution of so much heat, that the mass may become visibly red hot if too much water be not added.

When heated to a dull red heat in oxygen, or air, it takes up an additional atom of oxygen and forms the dioxide (see p. 162).

**Barium Hydroxide**, $Ba(HO)_2$, is obtained when the monoxide is slaked with water. It is manufactured by first heating the powdered native sulphate with coal, when a crude barium sulphide is formed. This is then heated in a stream of moist carbon dioxide, whereby it is converted into the carbonate, and superheated steam is then passed over the heated carbonate—

$$BaS + H_2O + CO_2 = BaCO_3 + H_2S$$
$$BaCO_3 + H_2O = Ba(HO)_2 + CO_2.$$

Barium hydroxide is soluble in water: the solution, known as *baryta-water*, absorbs carbon dioxide with the precipitation of barium carbonate.

The aqueous solution deposits crystals of hydrated barium hydroxide, $Ba(HO)_2,8H_2O$, in the form of colourless quadratic prisms, which on exposure to the air lose seven molecules of water.

Barium hydroxide, when heated in a current of air, yields barium dioxide.

Barium hydroxide was formerly employed in sugar-refining, but owing to its poisonous nature it has been superseded by strontium hydroxide (*q.v.*).

**Barium Dioxide** (*barium peroxide*), $BaO_2$.—This oxide is obtained by heating the monoxide to a low red heat in a stream of oxygen, or of air which has been deprived of atmospheric carbon dioxide.

The pure compound may be obtained by adding an excess of baryta-water to hydrogen peroxide, when hydrated barium peroxide separates out in crystalline scales—

$$Ba(HO)_2 + H_2O_2 + 6H_2O = BaO_2,8H_2O.$$

On drying in vacuo at 130° this compound loses water and is converted into the anhydrous peroxide.

The commercial peroxide may be purified by treatment with dilute hydrochloric acid, whereby barium chloride and hydrogen peroxide are formed. After the removal of insoluble impurities by filtration, baryta-water is cautiously added, which causes the precipitation of ferric oxide and silica. The liquid is then filtered, and to the clear liquid, consisting of a solution of barium chloride and hydrogen peroxide, an excess of strong baryta-water is added, when the hydrated barium peroxide is precipitated, as already explained.

Barium peroxide is a grey powder, which on being heated to a bright red heat gives up oxygen and forms the monoxide (p. 162).

Dilute acids decompose barium peroxide, with formation of hydrogen peroxide and a barium salt. Concentrated sulphuric acid forms barium sulphate and ozonised oxygen. When gently warmed in a stream of sulphur dioxide, the mass becomes incandescent and forms barium sulphate—

$$BaO_2 + SO_2 = BaSO_4.$$

**Barium Chloride,** $BaCl_2$, may be obtained by dissolving the natural carbonate in hydrochloric acid. It may be obtained from the natural sulphate, either by first converting it into the sulphide, and decomposing that with hydrochloric acid, or by roasting the mineral with powdered coal, limestone, and calcium chloride, when the following reactions take place—

$$BaSO_4 + 4C = BaS + 4CO$$
$$BaS + CaCl_2 = BaCl_2 + CaS.$$

The barium chloride is dissolved in water, and an insoluble oxysulphide of calcium remains.

Barium chloride forms colourless rhombic tables, $BaCl_2,2H_2O$, which at 15.6° are soluble to the extent of 43.5 parts in 100 parts of water. The salt is nearly insoluble in hydrochloric acid, and may therefore be precipitated from an aqueous solution by the addition of this acid.

Barium chloride, in common with all the soluble salts of this element, is highly poisonous.

**Barium Sulphate,** $BaSO_4$, is the most abundant naturally occurring barium compound. It is frequently met with as large rhombic crystals. The specific gravity of the mineral is 4.3 to 4.7; and on account of its high specific gravity, it received the name of *barytes*, or *heavy spar*.

It is formed as a heavy white precipitate, when sulphuric acid, or a soluble sulphate, is added to a solution of a barium salt. It is insoluble in water, and only very slightly soluble in dilute acids. It is soluble in hot concentrated sulphuric acid, especially when freshly precipitated; and the solution deposits, on cooling, an acid sulphate, $BaSO_4,H_2SO_4$. On exposure to moisture the solution deposits crystals of $BaSO_4,H_2SO_4,2H_2O$. Both of these compounds, in contact with water, yield insoluble normal barium sulphate and sulphuric acid.

Precipitated barium sulphate is latgely used as a pigment, known as *permanent white.*

**Barium Nitrate,** $Ba(NO_3)_2$, is obtained by dissolving the native carbonate, or the sulphide, in dilute nitric acid. It is also formed by double decomposition, when hot saturated solutions of sodium nitrate and barium chloride are mixed. The salt crystallises in large colourless octahedra belonging to the regular system. 100 parts of water at the ordinary temperature dissolve 9 parts, and at 100°, 32.2 parts of barium nitrate. When strongly heated, it is converted into barium oxide, with the evolution of nitrogen peroxide, oxygen, and nitrogen.

Barium nitrate is used in pyrotechny, in the preparation of mixtures for green fire.

**Barium Sulphide,** BaS, is obtained by methods analogous to those for preparing calcium sulphide (page 538), which it closely resembles in its properties.

# CHAPTER VII

## *ELEMENTS OF GROUP II. (FAMILY B.)*

| | |
|---|---|
| **Zinc, Zn** | 65 |
| **Cadmium, Cd** | 111.7 |
| **Mercury, Hg** | 199.8 |

THE three elements composing this family do not exhibit such a close resemblance to each other as exists between barium, strontium, and calcium; for although zinc and cadmium are very closely related, mercury in many respects differs widely from these, and from all the other elements in the same group.

Cadmium and zinc are almost invariably found associated together in nature, they are both fairly permanent in the air, and both readily take fire and burn, when strongly heated, forming the oxides. Both are acted upon by dilute hydrochloric and sulphuric acids, with evolution of hydrogen, and most of their salts are isomorphous.

Mercury is peculiar in being liquid at ordinary temperatures. Zinc and cadmium melt at 420° and 320° respectively, while mercury melts at $-38^\circ.8$. It is quite unacted upon by oxygen at ordinary temperatures, and combines with extreme slowness when heated. Its oxide, also, is readily decomposed by heat into its elements.

Dilute hydrochloric and sulphuric acids are entirely without action upon it, and it forms no hydroxide.

The hydroxide of zinc, $Zn(HO)_2$, differs from the corresponding cadmium compound, in being soluble in alkaline hydroxides.

These three elements resemble each other, and differ from those of family A of this group, in that they can be volatilised, mercury at a temperature about 357°, cadmium and zinc at temperatures approaching 1000°.

These three elements are also alike, in that their vapours consist of mono-atomic molecules.

## ZINC.

**Symbol, Zn. Atomic weight = 65.**

**Occurrence.**—Zinc is stated to have been found in Australia in the uncombined condition; with this exception, it is always met with in combination, chiefly as carbonate in *calamine* or *zinc-spar*, $ZnCO_3$, and as sulphide in *zinc-blende* or *black-jack*, ZnS. Other ores are *red zinc ore*, ZnO; and *franklinite*, $(ZnFe)O,Fe_2O_3$. *Gahnite*, or *zinc-spinnelle*, has the composition $ZnO,Al_2O_3$.

**Modes of Formation.**—The ores chiefly employed for the preparation of zinc are the carbonate and sulphide, although in New Jersey the red oxide and franklinite are used. The process consists of two operations, namely, first, the conversion of the ore into oxide of zinc, by calcination; and, second, the reduction of the oxide by means of coal at a high temperature. The calcination of the natural carbonate is readily accomplished, this compound merely giving up its carbon dioxide at the high temperature—

$$ZnCO_3 = ZnO + CO_2.$$

In the case of zinc blende, the operation consists in the oxidation of both the sulphur and the zinc by atmospheric oxygen, thus—

$$ZnS + 3O = ZnO + SO_2.$$

Considerable care has to be exercised in order to prevent the formation of zinc sulphate, which, in the subsequent operation, would be reconverted into sulphide, and so lost. The finely-crushed calcined ore is mixed with coke or coal, and heated to bright redness in earthenware retorts, when the oxide is reduced with the formation of carbon monoxide, and the metal distils and is collected in iron receivers. Zinc ores frequently contain small quantities of cadmium, and as this metal is more readily volatilised than zinc, it passes over in the first portions of the distilled product.

The two processes now almost exclusively in use for the reduction of zinc, known as the *Silesian* and the *Belgian* process,* differ only in metallurgical details, &c.

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* The old method, known as the *English process*, or *distillation per descensum*, is entirely obsolete. For details of this and all other metallurgical processes, the student is referred to treatises on metallurgy, such as Percy.

Commercial zinc usually contains carbon, iron, and lead, and occasionally arsenic and cadmium. It may be obtained in a higher degree of purity by careful distillation, but pure zinc is best obtained by first preparing the pure carbonate by precipitation, and then calcining and finally reducing with charcoal obtained from sugar.

**Properties.**—Zinc is a bluish-white, highly crystalline, and brittle metal. At a temperature of 300° it can be readily powdered in a mortar, while between 100° and 150° it admits of being drawn into wire or rolled into thin sheet. The presence of a small quantity of lead greatly enhances this property, but is detrimental when the zinc is required for making brass. Zinc which has been either rolled or drawn, no longer becomes brittle when cold, but retains its malleability.

Zinc melts at 420°, and when heated in air much beyond this point, the metal takes fire and burns with a bluish-white flame, the brilliancy of which becomes dazzling if a stream of oxygen be projected upon the burning mass. The product of its combustion is zinc oxide, ZnO, which forms a soft, white, flocculent substance resembling wool, and formerly known as *philosopher's wool.*

Zinc is permanent in dry air at ordinary temperatures, but when exposed to moist air it tarnishes superficially; it is also unattacked by water at the boiling temperature. It is soluble in a hot solution of sodium or potassium hydroxide, with evolution of hydrogen (p. 154).

Pure zinc is scarcely acted upon by pure sulphuric or hydrochloric acid, either dilute or strong. The presence of small quantities of impurities, however, determines the solution of the metal with the rapid evolution of hydrogen, hence ordinary commercial zinc is readily attacked by these acids, and also decomposes water at the boiling-point with the evolution of hydrogen.*

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* The difference between the behaviour of acids towards pure and commercial zinc, was formerly explained on the ground that the impurities present formed with the zinc a voltaic couple, whereby local electric currents were set up, while in the case of pure zinc no such action took place. The recent observations of Pullinger (Chem. Soc., 57) and Weeren (Berichte, 24) show that this is not a complete explanation. Weeren concludes that the insolubility of pure zinc in dilute acids, is due to the formation of a film of condensed hydrogen upon the surface of the metal, which stops all further action. The addition of oxidising agents, such as hydrogen peroxide, or dilute sulphuric acid which has been electrolysed, and therefore contains persulphuric acid, tends to destroy this film by oxidising the hydrogen, and therefore promotes the solution of the

Zinc is extensively used in the process of *galvanising* iron, which consists in coating iron with a film of zinc, not by electrical deposition, as would be implied by the name, but by dipping the iron into a bath of molten zinc. The layer of zinc preserves the iron from rusting. *Galvanised iron* is better able to withstand the action of air and moisture than tinned iron, hence it is extensively used for wire netting, corrugated roofing, water tanks, and other purposes where the metal is exposed to the oxidising influence of air and water.

**Alloys of Zinc.**—Zinc forms a number of useful alloys, the most important of which are the various forms of brass (see Copper). With certain metals, such as tin, copper, and antimony, zinc will mix in all proportions; while with others, such as lead and bismuth, it is only possible to obtain solid alloys of definite composition. When, therefore, lead and zinc are melted together, although in the molten condition the mixture is homogeneous, on cooling, the metals separate into two layers, the lighter zinc rising to the surface. The separation of the metals, however, is not perfect, for the zinc will have dissolved a certain quantity of the lead (1.2 per cent.), and the lower layer of lead is found to have dissolved a small proportion of zinc (1.6 per cent.), just as water and ether, when shaken together, separate into two layers, the uppermost being an ethereal solution of water, and the lower an aqueous solution of ether.

This property is made use of in the extraction of silver from lead (see p. 517).

The so-called *German silver*, or *nickel silver*, is a nearly white alloy of copper, nickel, and zinc.

Bronze coinage consists of 95 parts of copper, 4 of tin, and 1 of zinc, the small proportion of zinc giving to the alloy an increased hardness and durability.

**Zinc Oxide**, ZnO, the only oxide of zinc, occurs native as *red zinc ore*, the colour being due to the presence of manganese. It is formed as a soft white substance, when zinc is burnt in the air. It is manufactured under the name of *zinc white* by the combustion

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zinc. He also finds, that by mechanically removing this layer of hydrogen, either by constantly brushing the metallic surface or placing the materials under reduced pressure, the solution of the zinc by the acid is promoted. It is also found that the character of the surface of the metal, whether smooth or rough, affects the result; zinc that is unacted upon when its surface is perfectly smooth, is more readily attacked by the dilute acid when its surface is rough.

of zinc, the fumes being led into condensing-chambers, where the oxide collects.

Zinc oxide is a pure-white substance, which when heated becomes yellow, but again becomes white on cooling. When strongly heated in oxygen, it may be obtained in the form of hexagonal crystals; such crystals are occasionally found in the cooler parts of zinc furnaces. The oxide does not fuse in the oxyhydrogen flame, but, like lime, under these circumstances it becomes intensely incandescent; for some time after being so heated it appears phosphorescent in the dark. It is insoluble in water, and does not combine directly with water to form the hydroxide. It dissolves in acids, giving rise to the different zinc salts. Zinc oxide is largely used in the place of "white lead" as a pigment: although it does not equal white lead in covering power, or *body*, it possesses the advantage of not being blackened by exposure to atmospheric sulphuretted hydrogen.

**Zinc Hydroxide,** $Zn(HO)_2$, is formed as a white flocculent precipitate, when either sodium or potassium hydroxide, or a solution of ammonia, is added to a solution of zinc sulphate. The compound is soluble in an excess of either alkali, and is deposited from a strong solution in regular octahedra of the hydrated hydroxide, $Zn(HO)_2,H_2O$. Both of these compounds on heating, readily lose water, and are converted into the oxide.

**Zinc Chloride,** $ZnCl_2$, is formed by the direct combination of zinc with chlorine, or by the action of hydrochloric acid upon the metal. It is also obtained in the anhydrous state by distilling a mixture of mercuric chloride and zinc, or a mixture of anhydrous zinc sulphate and calcium chloride.

It is usually prepared on a large scale by dissolving zinc in hydrochloric acid, and after precipitating any manganese and iron, the liquid is boiled down in enamelled iron vessels, until on cooling it solidifies; it is usually cast into sticks.

Zinc chloride is a soft, white, easily fusible solid, which volatilises and distils without decomposition. It is extremely deliquescent, and readily soluble in water and in alcohol, its solution being powerfully caustic. From a strong aqueous solution, deliquescent crystals are deposited, having the composition $ZnCl_2,H_2O$.

When the aqueous solution is evaporated, partial decomposition takes place, hydrochloric acid being evolved, and basic compounds being precipitated, consisting of combinations of the chloride and oxide. Hence, during the concentration of the liquid in the preparation of zinc chloride, hydrochloric acid is added to re-dissolve this compound.

A paste made by moistening zinc oxide with zinc chloride, rapidly sets to a hard mass; this mixture, under the name of oxychloride of zinc, is employed in dentistry as a filling or stopping for teeth.

Zinc chloride unites with alkaline chlorides, forming a series of crystalline double salts having the general formula $ZnCl_2,2RCl$.

**Zinc Sulphate,** $ZnSO_4$, is formed when zinc is dissolved in sulphuric acid. It is obtained on a large scale by roasting the natural sulphide, whereby it is partially converted into the sulphate, which is then extracted with water.

The salt crystallises from its aqueous solution at ordinary temperatures in colourless rhombic prisms, $ZnSO_4,7H_2O$, isomorphous with $MgSO_4 7H_2O$. It is extremely soluble in water; 100 parts of water at the ordinary temperature dissolve 160 parts, and at 100°, 653.6 parts, of the crystalline salts. When exposed to the air, the crystals slowly effloresce, and if placed in vacuo over sulphuric acid, or if heated to 100°, they lose six molecules of water, leaving the monohydrated salt $ZnSO_4,H_2O$. At a temperature about 300° this is converted into the anhydrous compound, and at a white heat it gives off sulphur dioxide and oxygen, leaving the oxide.

The hydrated salt, $ZnSO_4,6H_2O$, is obtained in the form of monosymmetric crystals, when the salt is deposited at temperatures above 40°. This compound is isomorphous with $MgSO_4,6H_2O$.

Zinc sulphate combines with alkaline sulphates, forming a series of double salts, having the general formula $ZnSO_4,R_2SO_4,6H_2O$, which are also isomorphous with the corresponding magnesium compounds (page 531).

Zinc sulphate, in common with all the soluble salts of zinc, has an astringent taste, and is poisonous.

**Zinc Sulphide,** $ZnS$.—The natural compound, *zinc-blende*, is usually dark-brown or black, and exhibits crystalline forms belonging to the regular system. The mineral *wurtzite* is a less common variety of zinc sulphide, crystallising in hexagonal prisms. Zinc sulphide is obtained as a white amorphous precipitate, when an alkaline sulphide is added to a solution of a zinc salt, or when sulphuretted hydrogen is passed through an alkaline solution of a zinc salt.

Precipitated zinc sulphide is insoluble in acetic acid, but readily dissolves in dilute mineral acids, with evolution of sulphuretted hydrogen; hence the compound is not formed when sulphuretted hydrogen is passed through a solution of a zinc salt containing a free mineral acid.

**Zinc Carbonate,** $ZnCO_3$, is obtained as a white powder, when hydrogen sodium carbonate is added to a solution of zinc sulphate. If normal sodium carbonate be employed, the precipitated zinc compound consists of a basic carbonate, whose composition varies with the conditions of temperature and concentration of the liquids. A basic carbonate, having the composition $ZnCO_3,2Zn(HO)_2,H_2O$, is employed as a pharmaceutical preparation, under the name *zinci carbonas.*

## CADMIUM.

Symbol, Cd. Atomic weight = 111.7.

**Occurrence.**—Cadmium is never found in the uncombined state. The only natural compound of which cadmium is the chief constituent, is the extremely rare mineral *greenockite*, which is the sulphide, CdS. Cadmium occurs in small quantities in many zinc ores, such as the sulphide and carbonate; and in the process of extracting zinc from these ores, the cadmium is obtained in the first portions of the product of the distillation, partly as metal, and partly as oxide.

**Mode of Formation.**—The crude product of distillation is dissolved in dilute sulphuric or hydrochloric acid, and the cadmium precipitated as sulphide by means of sulphuretted hydrogen. The cadmium sulphide is then dissolved in strong hydrochloric acid, and precipitated as carbonate by means of ammonium carbonate. The washed and dried carbonate is first converted into oxide by calcination, and finally mixed with charcoal and distilled.

**Properties.**—Cadmium is a bluish-white metal resembling zinc in appearance, but much more malleable and ductile. It tarnishes superficially on exposure to the air, and, when strongly heated, burns with the formation of a brown smoke of cadmium oxide, CdO. The metal is attacked by dilute hydrochloric and sulphuric acids, with the evolution of hydrogen. It readily dissolves in nitric acid, yielding the nitrate, with the formation of oxides of nitrogen. Cadmium is less electro-positive than zinc, and is precipitated in the metallic condition from its solutions by that metal.

Cadmium melts at 320°, and when volatilised in an atmosphere of hydrogen, it forms crystals belonging to the regular system.

**Cadmium Oxide,** CdO, is formed as a brown fume or smoke, when cadmium burns in the air. It may be obtained by heating the carbonate or nitrate. That obtained by the ignition of the latter salt, is in the form of minute crystals, having a bluish-black appearance. Cadmium oxide is insoluble in water, but dissolves in acids yielding cadmium salts. It is infusible in the oxyhydrogen flame, but is readily reduced when heated on charcoal before the blowpipe; and the reduced metal, as it volatilises and burns, forms a characteristic brown incrustation of oxide upon the charcoal.

**Cadmium Chloride,** $CdCl_2$, is obtained by the action of hydrochloric acid upon the metal or the oxide. The salt is deposited from the solution in white silky crystals, having the composition, $CdCl_2,2H_2O$. On exposure to the air the crystals effloresce, and when heated become anhydrous.

**Cadmium Sulphide,** CdS, is obtained as a bright yellow precipitate, when sulphuretted hydrogen is passed through a solution of a cadmium salt. The precipitate is soluble in concentrated hydrochloric and nitric acids, and in warm dilute sulphuric acid. Cadmium sulphide is insoluble in ammonium sulphide; this property readily distinguishes it from arsenious sulphide, which in colour it closely resembles.

Cadmium sulphide is used as a pigment, both in oil and water-colours.

## MERCURY.

Symbol, Hg. Atomic weight = 199.8.

**Occurrence.**—In the uncombined state mercury is met with in small globules, disseminated through its ores, especially the sulphide. It is also occasionally found as an amalgam with silver and gold. The principal ore is *cinnabar*, HgS, and the chief mines of this ore are those of Almaden (Spain), Idria (Carniola), California, and the Bavarian Palatinate.

**Modes of Formation.**—Mercury may be obtained from the natural sulphides, by either roasting the ore, whereby the sulphur is oxidised to sulphur dioxide, and the metal liberated, or by distillation in closed retorts with lime, when calcium sulphide and sulphate are formed, and the mercury set free. The first method is almost exclusively employed.

At Idria the crude ore, consisting of cinnabar mixed with shale and earthy matters, is roasted in a furnace, upon perforated arches, *n*, *n'*; *p*, *p'*, Fig. 137. The action of the fire and heated air is to oxidise the sulphur, and volatilise the mercury, and the gases and vapours together pass through a series of flues or chambers, C, C, where the mercury condenses.

By the use of a reverberatory furnace (the Alberti furnace) the process can be made continuous. The ore is fed into the furnace through a hopper, and the calcined residue is raked out through an opening at the opposite end of the hearth. The gases are passed first through iron pipes, kept cool by water, and then through a series of chambers where the remaining metal is condensed.

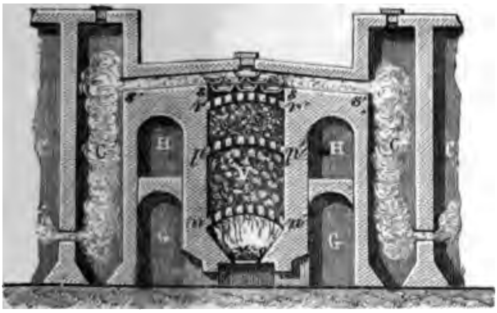

FIG. 137.

The method adopted at Almaden is essentially the same as the Idrian process, except that the condensation takes place in a series of pear-shaped earthenware vessels, called *aludels*, which are connected together as shown in Fig. 138. Usually six rows of forty-seven such aludels, are connected with six openings in a chamber immediately above the furnace.

FIG. 138.

The impure mercury is freed from mechanically mixed impurities by straining or filtering through chamois leather, but from metals in solution, such as zinc, tin, lead, and others, it is purified by distillation. For laboratory purposes, pure mercury is best obtained by distillation in vacuo, by means of the apparatus shown in Fig. 139 (Clarke). In this arrangement the mercury is distilled in a *Sprengel* vacuum. The mercury (previously cleaned by being thoroughly agitated with mercuric nitrate) is placed in the reservoir R, which is then placed upon the upper shelf S, and by means of the clamp, mercury is allowed to pass into the long wide tube T, and up into the bulb. The air in the tube and bulb escapes down the narrow inner tube, which reaches nearly to the top of the bulb, as seen in the enlarged detail, *t*. The mercury is allowed to rise in the bulb and fall down the long inner tube, after the manner of the Sprengel pump. The reservoir is then placed upon the lower

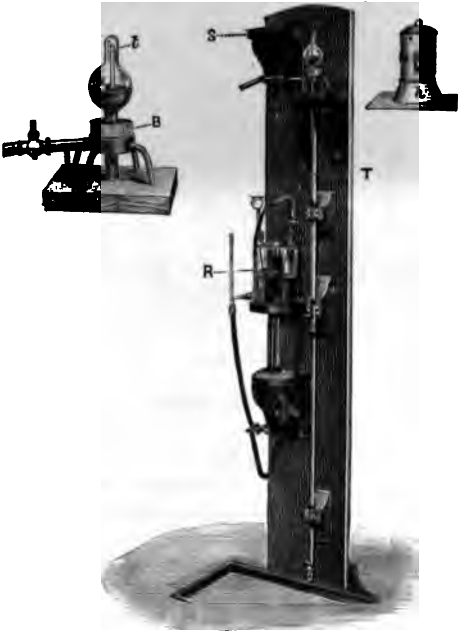

FIG. 139.

adjustable stand, and its height so arranged that the mercury in the bulb falls to the position shown in the figure. This space is a Torricellian vacuum. The mercury is then heated by a ring-burner, B, and the whole is protected from draught by the hood *h*. As the mercury distils, it passes down the inner tube, and by its fall continues to preserve the Sprengel vacuum within the bulb.

**Properties.**—At ordinary temperatures mercury is a bright, silver-white liquid metal (hence its old name *quicksilver*). When cooled to − 38.8° it solidifies to a highly crystalline solid, which is ductile and malleable, and softer than lead. When the liquid is cooled, it contracts uniformly until the solidifying point is reached, when considerable contraction takes place. Solid mercury, therefore, is denser than the liquid metal, and sinks in it. The specific gravity of liquid mercury at 0° is 13.596, while that of the solid at its melting-point is 14.193. Mercury in extremely thin films appears a violet colour by transmitted light.

Under a pressure of 760 mm. mercury boils at 357.25°, giving a colourless vapour. The density of mercury vapour referred to hydrogen is 100.93; hence this element, like its associates in the family to which it belongs, consists of mono-atomic molecules when in a state of vapour. Mercury gives off vapour even at ordinary temperatures, and a gold leaf suspended over mercury in a stoppered bottle, gradually becomes white upon the surface, owing to its amalgamation with the mercurial vapour.

The vapour of mercury is poisonous, giving rise to salivation.

Mercury does not tarnish on exposure to the air, and is unacted upon by a large number of gases: hence this liquid is invaluable to the chemist, affording a means of collecting and measuring gases which are soluble in water.

When submitted to prolonged heating in the air, it is slowly converted into the red oxide, which at a higher temperature is again decomposed into its elements.

Mercury is obtained in the form of a dull-grey powder, when it is shaken up with oil, or triturated with sugar, chalk, or lard. This operation is known as *deadening*, and is made use of in the preparation of mercurial ointment. The grey powder consists simply of very finely-divided mercury, in the form of minute globules.

Mercury is not attacked by hydrochloric acid. Strong sulphuric acid is without action upon it in the cold, but when heated the metal dissolves, with evolution of sulphur dioxide. Strong nitric acid rapidly attacks it, with formation of mercuric nitrate and oxides of nitrogen. Cold dilute nitric acid slowly dissolves it, forming mercurous nitrate.

**Alloys of Mercury.**—When mercury is one of the constituents of an alloy, the mixture is called an *amalgam*. Most metals will form an amalgam with mercury. In some cases, as with the alkali metals, the union is attended with great rise of temperature. In other cases, as with tin, an absorption of heat takes place.

Sodium and potassium amalgams are obtained by dissolving various amounts of the metals in mercury. In contact with water they are decomposed, hydrogen being evolved, and the alkaline hydroxide formed. On this account sodium amalgam is frequently used in the laboratory as a reducing agent. When heated to 440°, these amalgams leave behind crystalline compounds, $K_2Hg$ and $Na_2Hg$, which spontaneously inflame in contact with the air.

Zinc amalgams are only very slowly acted upon by dilute sulphuric acid; therefore, by the superficial amalgamation of the zinc plates used for galvanic batteries, the same result is obtained, as though the zinc were perfectly pure (see page 547), and no solution of zinc takes place until the electric circuit is closed.

Tin amalgams are employed for the construction of ordinary mirrors.

Amalgams of gold, and also copper and zinc, are used in dentistry as a filling or stopping for teeth.

**Oxides of Mercury.**—Two oxides are known, namely, mercurous oxide, $Hg_2O$, and mercuric oxide, $HgO$.

**Mercurous Oxide,** $Hg_2O$, is obtained as an unstable dark-brown or black powder, when sodium hydroxide is added to mercurous chloride. When exposed to the light, or when gently heated, it is converted into mercuric oxide and mercury.

**Mercuric Oxide,** $HgO$, is produced in small quantity by the prolonged heating of mercury in contact with air, or by igniting the nitrate. It is prepared on a large scale by heating an intimate mixture of mercuric nitrate and mercury. Obtained by these methods, it is a brick-red crystalline powder; but when sodium hydroxide is added to a solution of a mercuric salt, the oxide is precipitated as an orange-yellow amorphous powder. When heated, mercuric oxide first darkens in colour, and gradually becomes almost black, but returns to its original bright red colour on cooling. At a red heat it is completely decomposed into its elements.

**Salts of Mercury.**—Two series of salts, corresponding to the two oxides, are known—(*a*) *mercurous* salts, in which two atoms of the hydrogen of the acids are replaced by the divalent radical, or double atom ($Hg_2$); and ($\beta$) *mercuric* salts, in which the same amount of hydrogen is replaced by the single divalent atom ($Hg$). All the mercury salts are poisonous.

### (a) MERCUROUS SALTS.

**eurous Chloride,** $Hg_2Cl_2$ (*calomel*), is met with in small ties as the mineral *horn mercury*. It may be obtained by dition of sodium chloride, or hydrochloric acid, to a solution rcurous nitrate. On a large scale it is usually prepared by g. a mixture of mercuric chloride and mercury, when the rous chloride sublimes as a white or translucent fibrous

en a mixture of mercuric sulphate, common salt, and mercury ted, mercurous chloride is also obtained, thus—

$$HgSO_4 + 2NaCl + Hg = Na_2SO_4 + Hg_2Cl_2.$$

omel is perfectly tasteless, and is insoluble in water. When l, it vaporises without fusing. The density of the vapour s formed by heating mercurous chloride is 117.59, which is hat demanded by the formula $Hg_2Cl_2$. It has been shown, 'er, that the compound dissociates when vaporised, into ıric chloride and mercury.* Boiling hydrochloric acid de-ɔses mercurous chloride into mercury, which separates out, ıercuric chloride, which dissolves.

**rcurous Nitrate,** $Hg_2(NO_3)_2$, is deposited in the form of :less monosymmetric crystals containing $2H_2O$, from a solu-ıf mercury in cold dilute nitric acid. The salt is soluble in acidulated with nitric acid, but an excess of water causes :ecipitation of a basic nitrate having the composition—

$$Hg_2(NO_3)_2,Hg_2O,H_2O \text{ (or } 2Hg_2(NO_3)(HO)),$$

ı, on boiling, is converted into mercuric nitrate and mercury. her this or the normal salt, be boiled in the presence of an s of mercury, a basic nitrate of the composition—

$$Ig_2(NO_3)_2,2Hg_2O,2H_2O \text{ (or } Hg_2(NO_3)_2,4Hg_2(NO_3)(HO)),$$

ained.

**rcurous Sulphate,** $Hg_2SO_4$, is obtained as a white crystalline ɪitate, when dilute sulphuric acid is added to a solution of ırous nitrate. It is very slightly soluble in water.

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* Harris and Meyer. Berichte, June 1894.

### (β) MERCURIC SALTS.

**Mercuric Chloride,** $HgCl_2$ (*corrosive sublimate*), is formed when chlorine is passed over heated mercury. It is prepared on a large scale, by heating a mixture of mercuric sulphate and common salt; a small quantity of manganese dioxide being added, to prevent as far as possible, the formation of mercurous chloride. The mercuric chloride sublimes as a white translucent mass. It dissolves in water to the extent of 6.57 parts in 100 parts of water at 10°, and 54 parts in the same volume of water at 100°, forming an acid solution from which the salt is deposited in long white silky needles. It readily melts, and volatilises unchanged. It dissolves without decomposition in nitric acid, and in sulphuric acid, and volatilises unchanged from its solution in the latter acid on boiling.

Mercuric chloride is a violent poison: the best antidote is albumen, with which it forms an insoluble compound. It has also strong antiseptic properties, and on this account is largely used by taxidermists.

With hydrochloric acid, mercuric chloride forms two crystalline double chlorides, $HgCl_2,HCl$ and $2HgCl_2,HCl$; and with the alkaline chlorides it forms a number of similar double salts, of which the ammonium compound, $HgCl_2,2NH_4Cl,H_2O$, was known to the early chemists under the name *sal alembroth*.

**Mercuric Iodide,** $HgI_2$.—When mercury and iodine are rubbed together in a mortar, and moistened with a small quantity of alcohol, the red mercuric iodide is formed. It is also obtained by precipitation from a solution of mercuric chloride, upon the addition of potassium iodide. The precipitate first appears yellow, but in a few seconds becomes scarlet.

Mercuric iodide is insoluble in water, but readily dissolves in either mercuric chloride or potassium iodide, and also in alcohol and in nitric acid. From its solutions it is deposited in scarlet quadratic octahedra.

Mercuric iodide is dimorphous; when heated to about 150°, the scarlet quadratic crystals are changed into bright yellow rhombic prisms. At ordinary temperatures this yellow rhombic form is unstable, and on being lightly touched it is at once retransformed into the red quadratic form. At very low temperatures, however, the yellow variety is the more stable: thus, when the red crystals are exposed to the temperature of evaporating liquid oxygen, they pass into the yellow variety.

**Mercuric Nitrate,** $Hg(NO_3)_2$, is prepared by boiling nitric acid with mercury, until sodium chloride produces no precipitate with a sample of the liquid. If this solution be evaporated over sulphuric acid, deliquescent crystals are obtained of $2Hg(NO_3)_2,H_2O$, while the mother liquor has the composition $Hg(NO_3)_2,2H_2O$.

Mercuric nitrate exhibits a great tendency to form basic salts: thus, when this mother liquor is boiled, the compound $Hg(NO_3)_2,HgO,2H_2O$ is precipitated. When this compound, or the normal nitrate, is treated with an excess of cold water, there is formed the still more basic salt $Hg(NO_3),2HgO,H_2O$.

**Mercuric Sulphide,** $HgS$ (*cinnabar*).—When mercury and sulphur are triturated together in a mortar, or when excess of sulphuretted hydrogen is passed into a solution of a mercuric salt, mercuric sulphide is obtained as a black amorphous powder. If this be sublimed, it is obtained as a red crystalline substance.

Mercuric sulphide in the red condition, is also obtained by digesting the black amorphous product for some hours in alkaline sulphides. A soluble double sulphide is first formed, which when heated, is decomposed, with the deposition of red mercuric sulphide. This compound is manufactured on a large scale for use as the pigment *vermilion*.

Mercuric sulphide is insoluble in either nitric, hydrochloric, or sulphuric acid. In the presence of an alkali it is soluble in sodium or potassium sulphide, and deposits crystals from these solutions having the composition $HgS,Na_2S,8H_2O$, and $HgS,K_2S,5H_2O$ respectively.

**Ammoniacal Mercury Compounds.**—These may be regarded as ammonium salts, in which two atoms of hydrogen in ammonium ($NH_4$) have been replaced by either ($Hg_2$) in the *mercurous*, or by ($Hg$) in the *mercuric* compounds; the two atoms so replaced, being either drawn from one and the same ammonium group, or from two.

### (a) MERCUROUS COMPOUNDS.

**Mercurous Ammonium Chloride,** $(NH_2Hg_2)Cl$, is the black powder produced by the action of aqueous ammonia upon calomel, thus—

$$Hg_2Cl_2 + 2NH_3aq = (NH_2Hg_2)Cl + NH_4Cl\,aq.$$

**Mercurous Ammonium Nitrate,** $(NH_2Hg_2)NO_3$, is formed, together with other compounds, when aqueous ammonia is added to mercurous nitrate.

**Mercurous Diammonium Chloride,** $\left.\begin{matrix}NH_3Cl\\NH_3Cl\end{matrix}\right\}Hg_2$ or $(NH_3)_2Hg_2Cl_2$, is obtained when calomel absorbs dry gaseous ammonia. On exposure to the air, it gives up its ammonia, and is reconverted into mercurous chloride.

### (β) MERCURIC COMPOUNDS.

**Mercuric Ammonium Chloride,** $(NH_2Hg)Cl$ (*infusible white precipitate*), is formed when ammonia is added to a solution of mercuric chloride—

$$HgCl_2 + 2NH_3 = (NH_2Hg)Cl + NH_4Cl.$$

**Dimercuric Ammonium Chloride,** $(NHg_2)Cl$, is obtained by the action of water on the preceding compound.

**Mercuric Diammonium Chloride,** $\left.\begin{matrix}NH_3Cl\\NH_3Cl\end{matrix}\right\}Hg$, or $(NH_3)_2HgCl_2$ (*fusible white precipitate*), is obtained by adding mercuric chloride to a boiling aqueous solution of ammonium chloride and ammonia, until the precipitate which first forms, no longer dissolves. On cooling, the solution deposits small crystals belonging to the regular system.

**Oxy-dimercuric Ammonium Iodide,** $(NH_2Hg)I,HgO$, is produced by the action of aqueous ammonia upon mercuric iodide, thus—

$$4NH_3 + 2HgI_2 + H_2O = (NH_2Hg)I,HgO + 3NH_4I.$$

It is readily produced as a brown precipitate, by adding ammonia to a solution of mercuric iodide in potassium iodide containing an excess of potassium hydroxide.

The alkaline solution of potassium mercuric iodide is known as *Nestler's solution*, and constitutes a delicate reagent for detecting the presence of ammonia. Minute traces of free ammonia in solution produce a yellow or brown coloration with this test.

# CHAPTER VIII

## *THE ELEMENTS OF GROUP III*

| Family A. | | Family B. | |
|---|---|---|---|
| *Scandium*, Sc | 43.97 | Boron, B | 10.9 |
| *Yttrium*, Y | 89.6 | Aluminium, Al | 27.04 |
| *Lanthanum*, La | 138.5 | *Gallium*, Ga | 69.86 |
| *Ytterbium*, Yb | 173 | *Indium*, In | 113.4 |
| | | Thallium, Tl | 203.7 |

WITH the exception of boron, aluminium, and thallium, the members of this group are amongst the rarest of the elements.* Some of these occur only in minute traces in certain ores of other metals: such is the case with the elements gallium and indium, which are met with in certain specimens of zinc blende, the ore being considered *rich* in gallium if it contains as much as 0.002 per cent. of this element. Both gallium and indium were discovered by means of the spectroscope; the latter by Reich and Richter (1863), and named indium on account of two characteristic lines in the indigo-blue part of the spectrum; gallium by Lecocq de Boisbaudran (1875), and named after his own country. The spectrum of this metal is characterised by two violet lines. One of the most remarkable properties of gallium is its extremely low fusing-point, the metal melting at 30.15°. (For a comparison of the properties of gallium with Mendelejeff's *eka-aluminium*, see p. 109.)

Others of these elements are met with in certain rare minerals, thus, lanthanum occurs in the mineral *orthite* (from Greenland); and both yttrium and lanthanum (associated also with the rare elements cerium and erbium) are found in *gadolinite*, *or ytterbite* (from Ytterby).

**Boron** (the typical element of the group) is the only non-metal: all the others exhibit well-marked metallic properties. They all yield sesquioxides of the type $R_2O_3$; in the case of boron this oxide, $B_2O_3$, is acidic.

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* For detailed descriptions of the rare elements, the student is referred to larger treatises, or to chemical dictionaries.

Thallium in many respects is peculiar. It forms two series of compounds; in one class it functions as a monovalent, and in the other as a trivalent element. In some of its properties it exhibits a close analogy to the alkali metals; thus, it forms a soluble strongly alkaline hydroxide, TlHO, corresponding to KHO. And many of its salts, such as the sulphate, $Tl_2SO_4$; perchlorate, $TlClO_4$, and the phosphates, are isomorphous with the corresponding potassium compounds.

Thallium also shows many properties in common with lead, which in the periodic system is the next element in the series (the fourth long series). Thus, the chloride, like lead chloride, is thrown down as a white curdy precipitate on the addition of hydrochloric acid to a soluble salt of the metal, and like lead chloride, thallous chloride is soluble in hot water. Thallous iodide also closely resembles lead iodide, being formed as a yellow crystalline precipitate when potassium iodide is added to a soluble thallous salt.

Metallic thallium also bears the closest resemblance to metallic lead.

In the *thallic* compounds this element is more closely related to the other members of this family: thus thallic oxide, $Tl_2O_3$; thallic chloride, $TlCl_3$; and thallic sulphide, $Tl_2S_3$, are analogous to the corresponding boron compounds, $B_2O_3$, $BCl_3$, $B_2S_3$.

## BORON.

Symbol, B. Atomic weight = 10.9.

**Occurrence.**—The element boron has never been found in the free state. In combination it occurs principally as boric acid in volcanic steam, and as metallic borates, of which the commonest are *tincal*, a crude sodium borate, or borax, $Na_2B_4O_7$; *boracite* and *colemanite*, or *borate spar*, $Ca_2B_6O_{11}$; and *boronatrocalcite*, or *ulexite*, $Ca_2B_6O_{11}, Na_2B_4O_7, 16H_2O$.

**Modes of Formation.**—(1.) Boron may be prepared by heating boron trioxide with either sodium or potassium in a covered crucible—

$$B_2O_3 + 3K_2 = 3K_2O + 2B.$$

The fused mass is boiled with dilute hydrochloric acid, and the boron, which is in the form of a dark-brown powder, is separated by filtration.

(2.) The element may also be obtained by heating potassium borofluoride with potassium—

$$BF_3,KF + 3K = 4KF + B.$$

(3.) Boron is also formed when potassium is heated in the vapour of boron trichloride—

$$BCl_3 + 3K = 3KCl + B.$$

**Properties.**—Boron, as obtained by these methods, is a dark greenish-brown powder. When strongly heated in air it burns, uniting both with oxygen and nitrogen, forming a mixture of boron trioxide, $B_2O_3$, and boron nitride, BN. It is unacted upon by air at ordinary temperatures.

Boron has no action upon boiling water, but cold nitric acid converts it into boric acid—

$$B + 3HNO_3 = H_3BO_3 + 3NO_2.$$

When heated with sulphuric acid it is similarly oxidised—

$$2B + 3H_2SO_4 = B_2O_3 + 3SO_2 + 3H_2O.$$

When fused with alkaline carbonates, nitrates, sulphates, and hydroxides it forms borates of the alkali metals, thus—

$$\begin{aligned} 2B + 3Na_2CO_3 &= 2Na_3BO_3 = 3CO. \\ 2B + 6KHO &= 2K_3BO_3 = 3H_2. \end{aligned}$$

Boron dissolves in molten aluminium, which on cooling deposits crystals of a compound of aluminium and boron.*

**Boron Trioxide,** $B_2O_3$, is formed when boron burns in the air, or in oxygen. The readiest method for its preparation consists in heating boric acid to redness, when it fuses and gives up water—

$$2B(HO)_3 = 3H_2O + B_2O_3.$$

**Properties.**—The fused mass solidifies to a transparent, colourless, vitreous solid, which gradually absorbs atmospheric moisture, and becomes opaque. It is not volatile below a white heat, and on this account, although only a feeble acid, it is capable at high temperatures of displacing strong acids which are volatile, from their combinations; thus, when boron trioxide is fused with potassium sulphate, potassium borate is formed, and sulphur trioxide expelled—

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* This compound was at one time mistaken for an allotropic modification of boron.

$$B_2O_3 + 3K_2SO_4 = 2B(KO)_3 + 3SO_3.$$

Boron trioxide at a high temperature is capable of dissolving many metallic oxides, some of which impart to the fused mass a characteristic colour.

Boron forms three oxyacids, namely—

Orthoboric acid, $B(HO)_3$, or $H_3BO_3$.
Metaboric acid, $B_2O_2(HO)_2$, or $H_2B_2O_4$, or $B_2O_3,H_2O$.
Pyroboric acid, $B_4O_5(HO)_2$, or $H_2B_4O_7$, or $2B_2O_3,H_2O$.

**Orthoboric Acid,** or **Boric Acid,** $B(HO)_3$, occurs naturally, both in the waters and in the jets of steam which issue from the ground in many volcanic districts, notably in Tuscany.

The actual amount of boric acid in these natural jets of steam, or *soffioni*, is very small; but as the steam becomes condensed in the pools of water, or *lagoons*, which often surround the jets, the amount of boric acid with which the water becomes charged, is sufficient to constitute this a profitable source of supply. To obtain the acid, large brick-work basins are built round the steam jets, in such a manner that the liquid can be caused to flow from one to another. Water is placed in the highest basin, and, after the steam from the fumaroles beneath it has blown through for twenty-four hours, the liquid is passed on to the second basin, and a fresh supply of water is run into the first. In this way the water passes on through a series of four or five such basins, receiving the steam of the soffioni for twenty-four hours in each. The muddy liquor, after passing through a settling reservoir, is concentrated by evaporation, the heat from the natural steam being utilised. The concentrated liquor, having a specific gravity about 1.07, is allowed to cool in lead-lined tanks; and the crystals, after being drained, are dried upon the floor of a chamber, also heated by the natural steam. The crude boric acid thus obtained, is purified by recrystallisation.

Boric acid may be prepared by the action of sulphuric acid, or hydrochloric acid, upon a strong solution of borax—

$$Na_2B_4O_7 + 5H_2O + 2HCl = 2NaCl + 4H_3BO_3.$$

**Properties.**—Boric acid crystallises in lustrous white laminæ, which are soft and soapy to the touch. 100 parts of water at 18° dissolve 3.9 parts of the acid. The aqueous solution turns blue litmus to a port wine red, similar to the colour produced by carbonic acid. In contact with turmeric paper, it gives a brown stain, resembling that caused by alkalies, but readily distinguished by not being destroyed by acids, and by being turned black in contact with a solution of sodium hydroxide. Boric acid is more soluble in alcohol than in water; and when this solution is boiled, a portion of the boric acid volatilises with the alcohol, and imparts a green colour to the flame of the burning vapour.

The orthoborates are mostly unstable salts.

**Metaboric Acid,** $H_2B_2O_4$, is obtained when boric acid is heated to 100°—

$$2H_3BO_3 = 2H_2O + H_2B_2O_4.$$

The metaborates are more stable salts than the orthoborates. The acid is dibasic, and forms normal and acid salts, as well as super-acid salts, thus—

| | |
|---|---|
| Normal potassium metaborate | $K_2B_2O_4$. |
| Acid potassium metaborate | $HKB_2O_4$. |
| Super-acid potassium metaborate | $HKB_2O_4,H_2B_2O_4$. |

**Pyroboric Acid,** $H_2B_4O_7$, is obtained by heating either metaboric acid, or orthoboric acid, to 140° for some time—

$$2H_2B_2O_4 = H_2O + H_2B_4O_7.$$
$$4H_3BO_3 = 5H_2O + H_2B_4O_7.$$

**Borax.**—The most important salt of pyroboric acid is the sodium salt, ordinary borax, $Na_2B_4O_7$. This compound occurs naturally as the mineral *tincal.* It is manufactured from boric acid by double decomposition with sodium carbonate—

$$4H_3BO_3 + Na_2CO_3 = Na_2B_4O_7 + 6H_2O + CO_2.$$

Anhydrous sodium carbonate is added to a boiling solution of boric acid, and the liquid is then allowed to crystallise, when it forms large transparent prisms belonging to the mono-symmetric system, of the composition $Na_2B_4O_7,10H_2O$.

Borax is also obtained from the natural calcium borate, which has the composition $Ca_2B_6O_{11}$. The powdered mineral is boiled with water, and soda ash is added to the mixture, when calcium carbonate is precipitated, and a mixture of borax and sodium metaborate is formed—

$$Ca_2B_6O_{11} + 2Na_2CO_3 = 2CaCO_3 + Na_2B_4O_7 + Na_2B_2O_4.$$

On crystallisation, the borax deposits, and the more soluble metaborate remains in the mother liquor. On concentrating these mother liquors, and blowing carbon dioxide through the solution, the metaborate is converted into borax, which is precipitated as a fine meal, leaving sodium carbonate in solution—

$$2Na_2B_2O_4 + CO_2 = Na_2CO_3 + Na_2B_4O_7.$$

When heated, borax loses its water of crystallisation, and swells up, forming a white porous mass, which finally melts to a clear glass.

One hundred parts of water at 10° dissolve 4.6 parts of crystallised borax, and at 100°, 201.4 parts; the solution possesses a feeble acid reaction.

When deposited slowly from warm solutions, borax crystallises in octahedra belonging to the regular system, and having the composition $Na_2B_4O_7,5H_2O$.

**Boron Trifluoride,** $BF_3$, is formed when boron is brought into fluorine: the boron takes fire spontaneously in the gas, forming the trifluoride.

It is also produced when a mixture of dry powdered fluorspar and boron trioxide is heated to redness in an iron vessel, calcium borate being at the same time produced—

$$2B_2O_3 + 3CaF_2 = Ca_3B_2O_6 + 2BF_3.$$

It is more conveniently prepared by heating together fluorspar, boron trioxide, and sulphuric acid. The reaction may be regarded as taking place in two stages, thus—

(1.) $CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$
(2.) $B_2O_3 + 6HF = 3H_2O + 2BF_3.$

**Properties.**—Boron trifluoride is a colourless, pungent-smelling gas, which fumes strongly in moist air on account of its powerful affinity for water. So great is this affinity, that a strip of paper introduced into the gas is charred, by the abstraction of the elements of water.

Boron fluoride neither burns, nor supports the combustion of ordinary combustibles. When potassium is heated in the gas, it burns brilliantly, forming the borofluoride.

At 0° one volume of water dissolves about 1000 volumes of the gas, the absorption being attended with rise of temperature.

When the gas is passed into water until the solution is distinctly acid, a mixture of metaboric acid and hydrofluoboric acid is obtained; the former separates out, while the latter remains in solution—

$$8BF_3 + 4H_2O = H_2B_2O_4 + 6HBF_4.$$

When the gas is passed into water until the latter is saturated, a syrup-like liquid is obtained which chars organic matter and is strongly corrosive. This liquid is sometimes called fluoboric acid, and contains boron trifluoride and water in the proportions represented by the formula $2BF_3,4H_2O$; or it may be regarded as consisting of metaboric acid and hydrofluoric acid, as expressed by the formula $H_2B_2O_4,6HF$.* In presence of an excess of water, this substance is decomposed into metaboric acid and hydrofluoboric acid.

When mixed with its own volume of dry ammonia gas, boron fluoride forms a white crystalline compound, having the composition represented by the formula $BF_3,NH_3$. This substance may be sublimed without change. Two other compounds with ammonia are known, namely $BF_3,2HN_3$, and $BF_3,3NH_3$. These are both colourless liquids, which on being heated give off ammonia, leaving the solid $BF_3,NH_3$.

The salts of hydrofluoboric acid, $HBF_4$, are known as *borofluorides*, and are formed by the action of the acid upon metallic hydroxides—

$$HBF_4 + KHO = H_2O + KBF_4.$$

In many instances, their aqueous solutions redden litmus; this is the case with ammonium borofluoride, $NH_4BF_4$, and calcium borofluoride, $Ca(BF_4)_2$.

**Boron Trichloride**, $BCl_3$, is produced when boron is heated in a stream of dry chlorine.

It is most readily prepared by passing dry chlorine over an intimate mixture of boron trioxide and charcoal, heated to redness in a porcelain tube. The volatile product is condensed in a tube immersed in a freezing mixture—

$$B_2O_3 + 3Cl_2 + 3C = 3CO + 2BCl_3.$$

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* It is considered very doubtful whether this substance can be regarded as a definite compound.

**Properties.**—Boron trichloride is a mobile, colourless liquid, boiling at 18.23°. It fumes in moist air, being decomposed in contact with water, with formation of boric and hydrochloric acids—

$$BCl_3 + 3H_2O = B(HO)_3 + 3HCl.$$

Boron trichloride unites directly with dry gaseous ammonia, with evolution of considerable heat, forming a white crystalline compound, having the composition $2BCl_3,3NH_3$.

**Boron Hydride**, $BH_3$.—This compound has never been obtained in a state of purity. When magnesium boride (an impure substance obtained by fusing boron trioxide and magnesium in a covered crucible) is acted upon by hydrochloric acid, a gas is evolved which has a characteristic and unpleasant smell, and which produces headache and sickness when inhaled. The gas is largely hydrogen, containing, however, a certain quantity of boron hydride, which imparts to the flame a green colour, and produces boron trioxide. When passed through a heated tube, boron is deposited as a brown film. When burnt with a limited supply of air, or when a cold porcelain dish is depressed into the flame of the burning gas, a brown stain of boron is deposited.

**Boron Nitride**, BN, is formed when boron is strongly heated in nitrogen or in ammonia. It is best obtained by heating, in a covered platinum crucible, a mixture of one part of dehydrated borax, and two parts of ammonium chloride—

$$Na_2B_4O_7 + 2NH_4Cl = 2BN + B_2O_3 + 2NaCl + 4H_2O.$$

Boron nitride is a white amorphous powder. It is insoluble in water, but is slowly acted upon by boiling caustic alkalies, with evolution of ammonia—

$$BN + 3KHO = K_3BO_3 + NH_3.$$

Heated in a current of steam it forms boron trioxide and ammonia—

$$2BN + 3H_2O = B_2O_3 + 2NH_3.$$

**Boron Sulphide**, $B_2S_3$ is prepared by heating a mixture of boron trioxide and carbon (made by mixing boron trioxide and soot with oil, and heating the pellets out of contact with air) to bright redness in a stream of vapour of carbon disulphide—

$$2B_2O_3 + 3C + 3CS_2 = 6CO + 2B_2S_3.$$

Boron sulphide is a yellowish solid, consisting of small crystals. It has a strong unpleasant smell, and its vapour attacks the eyes. It is immediately decomposed by water, being converted into boric acid and sulphuretted hydrogen—

$$B_2S_3 + 6H_2O = 2B(HO)_3 + 3H_2S.$$

## ALUMINIUM.

Symbol, Al. Atomic weight = 27.04.

**Occurrence.**—Aluminium is one of the most abundant of all the elements, although it has never been found in the uncombined state. In combination with oxygen as $Al_2O_3$, it constitutes such minerals as *corundum*, *ruby*, *sapphire*. As the hydrated oxide, $Al_2O_3,H_2O$, it occurs associated with iron oxide in the mineral *bauxite*, which constitutes the chief source from which the metal itself is obtained. As a double fluoride of aluminium and sodium, $Al_2F_6,6NaF$, it occurs in the mineral *cryolite*, and as a hydrated phosphate in the various forms of *turquoise*. Aluminium is met with in enormous quantities in the form of silicate, constituting the various *clays*; and as compound silicates in the *felspars*, and other common minerals constituting a large proportion of the solid crust of the earth.

**Mode of Formation.**—Aluminium is prepared on a large scale from the mineral bauxite, the process being conducted in four stages :—(1.) and (2.) The preparation of pure aluminium oxide, free from iron. (3.) The preparation of a double chloride of aluminium and sodium. (4.) The reduction of the double chloride by means of sodium.

(1.) The powdered bauxite (usually containing about 50 per cent. of alumina) is mixed with sodium carbonate and heated for five or six hours in a reverberatory furnace, when carbon dioxide is evolved and sodium aluminate is formed—

$$Al_2O_3 + 3Na_2CO_3 = Al_2O_3,3Na_2O + 3CO_2.$$

(2.) The sodium aluminate is extracted with water, leaving the iron in the form of insoluble oxide. Through the filtered liquid a stream of carbon dioxide is then passed, which decomposes the sodium aluminate, regenerating sodium carbonate, and precipitating hydrated aluminium oxide—

$$Al_2O_3,3Na_2O + 3H_2O + 3CO_2 = 3Na_2CO_3 + Al_2O_3,3H_2O.$$

(3.) The purified alumina, after being washed and dried, is mixed with sodium chloride and powdered wood charcoal, and sufficient water added to enable the mixture to be worked up into balls. These are dried at 150° and then packed into a vertical fireclay cylinder, where they are heated to bright redness in a stream of chlorine, when the following reaction takes place—

$$Al_2O_3 + 3C + 3Cl_2 = 3CO + Al_2Cl_6.$$

The aluminium chloride combines with the sodium chloride present in the mixture, forming the double chloride, $Al_2Cl_6,2NaCl$, which volatilises from the retort, and is condensed in an earthenware receiver as a nearly white crystalline salt, which is almost entirely free from iron.

(4.) In order to reduce the double chloride, three charges (each consisting of a mixture of 25 kilos of the salt, 11 kilos of powdered cryolite (as a flux), and 12 kilos of metallic sodium in small pieces) are thrown into a strongly heated reverberatory furnace, and are immediately followed by a fourth charge, containing the same quantity of the double chloride and of cryolite, but without sodium. A violent reaction at first takes place, and after a short time the entire mass is in a state of fusion, the metal separating out beneath the slag—

$$Al_2Cl_6,2NaCl + 6Na = 2Al + 8NaCl.$$

**Properties.**—Aluminium is a tin-white metal, possessing great tensile strength. It is very ductile and malleable, but requires frequent annealing during the process of drawing or hammering. Its specific gravity is 2.58; by hammering and rolling it may be raised to 2.68. Its power of conducting heat and electricity is about one-third that of silver. Aluminium is an extremely sonorous metal, and when struck it emits a clear and sustained note. It is not tarnished by air under ordinary circumstances, but when strongly heated it becomes oxidised; and in the condition of thin foil it readily burns in oxygen, forming alumina, $Al_2O_3$. The metal melts at a temperature about 700°. Aluminium is scarcely acted upon by nitric acid of any strength, but readily dissolves in hydrochloric acid, and in solutions of sodium or potassium hydroxide with elimination of hydrogen. When heated with strong sulphuric acid, aluminium sulphate is formed, and sulphur dioxide is evolved—

$$2Al + 6H_2SO_4 = Al_2(SO_4)_3 + 6H_2O + 3SO_2.$$

Organic acids are almost without action upon aluminium, but in the presence of sodium chloride they are capable of dissolving it to a slight extent. Pure aluminium is scarcely acted upon by water or steam, but the presence of impurities such as usually occur in the commercial metal, renders it much more readily oxidised.

Aluminium is a highly electro-positive element, and is capable of reducing a number of other metals from their combinations with oxygen or sulphur. Thus, when finely divided aluminium is heated with the oxides of such metals as manganese, chromium, tungsten, uranium, along with lime to form a slag, an energetic action takes place, in which the aluminium combines with the oxygen, and the metals are thrown out of combination, and are obtained as a coherent mass. Similarly, iron pyrites is reduced to the condition of metallic iron, with the formation of aluminium sulphide.

**Alloys of Aluminium.**—The most important of these is an alloy with copper, containing 10 per cent. of aluminium, and known as *aluminium bronze*. This alloy has a yellow colour, resembling that of gold; it is scarcely tarnished by exposure to air, and is susceptible of a high polish. Its specific gravity is 7.69, and it possesses a tenacity equal to that of steel, and more than twice that of the best gun-metal. The alloy is malleable, and yields good castings, and on account of its many valuable properties it is employed for a variety of purposes.

**Aluminium Oxide** (*alumina*), $Al_2O_3$, occurs native in a colourless crystalline condition as *corundum*, and coloured by traces of various metallic oxides in such precious stones as *ruby*, *sapphire*, and *amethyst*. In a less pure condition, it occurs in large quantities as *emery*. These naturally occurring crystalline forms of alumina are extremely hard, ranking second only to *diamond*. Alumina is obtained in an amorphous condition, by igniting either the precipitated hydroxide, or ammonia alum, thus—

$$Al_2(HO)_6 = 3H_2O + Al_2O_3.$$
$$Al_2(SO_4)_3(NH_4)_2SO_4 = 2NH_3 + H_2O + 4SO_3 + Al_2O_3.$$

It is also obtained by the action of carbon dioxide upon sodium aluminate (p. 569). In the crystalline form it is obtained by strongly heating a mixture of aluminium fluoride and boron trioxide—

$$Al_2F_6 + B_2O_3 = Al_2O_3 + 2BF_3.$$

The boron trifluoride volatilises, leaving alumina in the form of rhombohedral crystals. Artificial rubies have been obtained by heating barium fluoride with alumina, and adding a trace of potassium dichromate.

Amorphous alumina is a soft white powder, insoluble in water, but dissolved by acids with the formation of aluminium salts; after being strongly heated, however, alumina is attacked only with slowness by hydrochloric or sulphuric acid.

**Aluminium Hydroxides.**—Three hydroxides, or hydrated oxides, are known. Thus, when ammonia is added to a solution of an aluminium salt, a white gelatinous precipitate is obtained, which when dried at 100° consists of the trihydrate, $Al_2O_3,3H_2O$, or $Al_2(HO)_6$. If this be heated to 300° it loses $2H_2O$, and is converted into the mono-hydrate, $Al_2O_3,H_2O$, or $Al_2O_2(HO)_2$. By the addition of ammonia to a boiling solution of an aluminium salt and drying the precipitate at 100°, the dihydrate is obtained, $Al_2O_3,2H_2O$, or $Al_2O(HO)_4$.

These compounds are soluble in acids, and all yield the same aluminium salts.

Aluminium hydroxide unites with many soluble organic colouring-matters, and precipitates them from solution as *lakes*. Upon this property depends the use of aluminium salts as *mordants* in dyeing and calico printing: the colouring-matter being held in the fibres of the material by the aluminium hydroxide, which is previously precipitated upon the fabric.

**Aluminates.**—Alumina is capable of acting as a feeble acidic oxide: thus, the hydroxides are dissolved by sodium or potassium hydroxide, yielding salts known as aluminates. Certain aluminates occur native, such as *spinelle* (magnesium aluminate), $Al_2O_3,MgO$, and chrysoberyl (beryllium aluminate), $Al_2O_3,BeO$. Sodium aluminate is now manufactured on a large scale, for the preparation of the metal (p. 569) and also of aluminium salts.

It is readily decomposed even by carbonic acid (p. 569), and by aluminium chloride—

$$Al_2O_3,3Na_2O + Al_2Cl_6 = 6NaCl + 2Al_2O_3.$$

On the manufacturing scale powdered cryolite is employed to effect this decomposition, the aluminium hydroxide being precipitated, and the sodium fluoride going into solution—

$$Al_2O_3,3Na_2O + Al_2F_6,6\ aF = 12NaF + 2Al_2O_3.$$

**Aluminium Sulphate**, $Al_2(SO_4)_3,18H_2O$, is found native as the minerals *hair salt* and *aluminite*, the latter being a basic salt having the composition $Al_2O_3SO_3,9H_2O$. The normal sulphate is obtained by dissolving the hydrated oxide in sulphuric acid. Large quantities of commercial aluminium sulphate are made, by directly dissolving bauxite in sulphuric acid. The product, however, contains iron, which is detrimental to the technical uses to which the sulphate is applied, and from which therefore it must be carefully purified. Pure aluminium sulphate is prepared from either bauxite, or cryolite, by first forming sodium aluminate: in the former case by heating the mineral with sodium carbonate (p. 569), and in the case of cryolite by boiling with milk of lime—

$$Al_2F_6,6NaF + 6Ca(HO)_2 = 6CaF_2 + 6H_2O + Al_2O_3,3Na_2O.$$

The sodium aluminate, free from iron, is then decomposed by carbon dioxide, as already described, and the precipitated hydrated oxide dissolved in sulphuric acid. On concentration, the mass solidifies to a white, difficultly crystallisable solid.

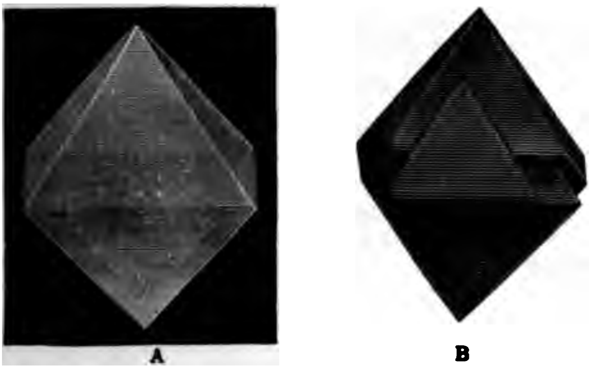

FIG. 140.

**The Alums.**—Aluminium sulphate unites with certain other sulphates, forming double salts, which belong to a class of compounds known as the alums. The most important of these compounds is the double sulphate of aluminium and potassium, $Al_2(SO_4)_3,K_2SO_4,24H_2O$, known as *potassium alum*, or simply *alum*.

The alums have the general formula $R_2(SO_4)_3,M_2SO_4,24H_2O$, in which R may be either aluminium, iron, chromium, manganese (indium or gallium), and M a monovalent element or group, such as sodium, potassium, or ammonium.

These compounds are all isomorphous, crystallising in the regular system (usually in cubes or octahedra) with twenty-four molecules of water. Fig. 140 represents a crystal of potassium alum (A) and potassium chromium alum (B). In naming the alums* it is usual, when the salt contains *aluminium*, only to introduce the name of the monovalent element or group: thus, *ammonium alum*, or *potassium alum*, signifies the double sulphate of ammonium, or potassium, and aluminium. If, on the other hand, the compound contains no aluminium, the names of both metals are used, thus, *potassium chromium alum*, *ammonium iron alum*.

A second class of double sulphates is known, which resemble the alums, although they are not isomorphous with them. These are termed *pseudo-alums*. They may be regarded as alums, in which the two atoms of the monovalent element are replaced by one atom of a divalent element, thus—

| | |
|---|---|
| Manganese aluminium, pseudo-alum | $Al_2(SO_4)_3MnSO_4,24H_2O$. |
| Iron aluminium, pseudo-alum | $Al_2(SO_4)_3FeSO_4,24H_2O$. |
| Copper iron, pseudo-alum | $Fe_2(SO_4)_3CuSO_4,24H_2O$. |
| Zinc iron, pseudo-alum | $Fe_2(SO_4)_3ZnSO_4,24H_2O$. |
| Magnesium manganese, pseudo-alum | $Mn_2(SO_4)_3MgSO_4,24H_2O$. |

The alums are all soluble in water, and their solutions have an acid reaction and possess an astringent taste. When heated, they gradually part with water, and at higher temperatures are broken up into oxides and alkaline sulphates; in the case of ammonium alums, leaving only the metallic oxide.

**Potassium Alum,** $Al_2(SO_4)_3,K_2SO_4,24H_2O$, is prepared by the addition of the requisite quantity of potassium sulphate to aluminium sulphate. A considerable quantity of alum is also obtained from a naturally occurring basic potassium alum, known as *alum stone*, or *alunite*, which has the composition $Al_2(SO_4)_3$, $K_2SO_4,2Al_2O_3,8H_2O$. At Tolfa this is first calcined, and afterwards lixiviated with water, which dissolves the potassium alum, leaving alumina undissolved. The alum so obtained is known as *Roman alum;* and although it has a reddish colour, due to the presence of iron, this iron is present only as the insoluble oxide, which is readily removed, and the salt is in reality extremely pure.

---

* Selenic acid (the selenium analogue of sulphuric acid) forms a similarly constituted series of double selenates, crystallising in the same form, and with the same number of molecules of water. The system of nomenclature adopted for these compounds is the same: thus, *ammonium selenio-alum* signifies the double selenate of ammonium and aluminium, while *potassium chromium selenio-alum* represents the double selenate of potassium and chromium.

Alunite is also converted into alum, by treating the calcined mineral with sulphuric acid, and adding the requisite quantity of potassium sulphate. A large quantity of alum is manufactured from *alum shale*, which is a bituminous mineral, consisting chiefly of aluminium silicate, with finely-divided iron pyrites disseminated throughout the mass. The shale is usually first roasted, and is then exposed to the action of air and moisture, whereby the oxidation of the pyrites is completed. The result of this oxidation is the formation of sulphuric acid, which, acting upon the aluminium silicate, forms aluminium sulphate, while the iron is converted into ferrous and ferric sulphates, and ferric oxide. The oxidised mass is then lixiviated with water, and, after concentration, the requisite quantity of potassium chloride or sulphate is added to the hot liquor. (The use of potassium chloride is preferable, as by double decomposition the ferrous and ferric sulphates are converted into the very soluble chlorides, and an equivalent amount of potassium sulphate is formed.) The liquor is stirred mechanically during its cooling, whereby the alum is deposited in small crystals known as *alum meal*, which permit of its more ready purification by recrystallisation.

Alum crystallises in fine colourless regular octahedra, which, on exposure to the air, become coated with a white efflorescene, due not to loss of water, but to absorption of atmospheric ammonia, and the formation of a basic salt.

The solubility of alum in water increases rapidly with rise of temperature. Thus, 100 parts of water at 0° dissolve 3.9 parts of alum; at 50°, 44.1 parts; and at 100°, 357.5 parts. Alum is insoluble in alcohol.

When heated to 42°, alum loses 11 molecules of water; and when heated to 61° in a closed vessel over sulphuric acid, it parts with 18 molecules.

On the application of heat, alum first melts in its own water of crystallisation, which is gradually expelled, until at a dull red heat the salt is converted into a white porous mass, known as *burnt alum*. At a still higher temperature it is broken up into potassium sulphate, alumina, and sulphur trioxide. Burnt alum is only very slowly dissolved by water. The chief use of alum is as a mordant in dyeing, alum being a salt which is much more easily obtained in a state of purity than aluminium sulphate. By the addition of sodium hydroxide or carbonate to a solution of alum, until the precipitate first thrown down is just redissolved, two-thirds of the sulphuric acid, in combination with the aluminium, becomes converted into sodium sulphate; and the solution, which is no longer acid, contains a basic alum, known as *neutral alum*—

$$Al_2(SO_4)_3,K_2SO_4 + 6NaHO = Al_2SO_6,K_2SO_4 + 3Na_2SO_4 + 3H_2O.$$

This solution gives up its alumina to the fabric with great ease, and on this account is used by dyers and calico printers as a mordant.

**Aluminium Fluoride, $Al_2F_6$.**—This compound may be prepared by passing gaseous hydrochloric acid over a mixture of fluorspar and alumina heated to whiteness in a graphite tube, when aluminium fluoride volatilises, leaving calcium chloride—

$$3CaF_2 + Al_2O_3 + 6HCl = 3H_2O + 3CaCl_2 + Al_2F_6.$$

In the form of a crystalline hydrate it may be obtained by dissolving alumina in aqueous hydrofluoric acid—

$$Al_2O_3 + 6HF + H_2O = Al_2F_6,7H_2O.$$

Aluminium fluoride forms colourless rhombohedral crystals, which are insoluble in water. It combines with alkali fluorides, forming insoluble double fluorides, of which the sodium compound is the most important, $Al_2F_6,6NaF$. This compound occurs native as the mineral *cryolite.*

**Aluminium Chloride,** $Al_2Cl_6$.—This compound is produced when powdered aluminium is strongly heated in chlorine, or with certain metallic chlorides, such as zinc chloride. It is best obtained by passing chlorine over a strongly-heated mixture of alumina and charcoal.

An aqueous solution of aluminium chloride may be obtained by dissolving alumina in hydrochloric acid. On evaporation, the solution deposits crystals of a hydrate, $Al_2Cl_6,12H_2O$.

Aluminium chloride forms white hexagonal crystals, which fume strongly in moist air. When gently heated it vaporises, and sublimes without fusion. When heated under pressure of its own vapour, the compound melts. It dissolves in water with the evolution of heat, and the solution, on evaporation, deposits the hydrated chloride, which, on being heated, breaks up into hydrochloric acid, water, and alumina—

$$Al_2Cl_6,12H_2O = 6HCl + 9H_2O + Al_2O_3.$$

Aluminium chloride unites with other metallic chlorides, forming double salts, of which the sodium compound $Al_2Cl_6,2NaCl$ (page 570) is the most important. It also combines with ammonia, forming the compounds $Al_2Cl_6 6NH_3$ and $Al_2Cl_6 2NH_3$.

**Aluminium Sulphide,** $Al_2S_3$.—When finely divided aluminium is heated with iron pyrites, an energetic reaction takes place; metallic iron being reduced, and aluminium sulphide being formed. The same compound is produced when sulphur is thrown upon strongly heated aluminium. As obtained by these methods, aluminium sulphide is a greyish black solid, which, when thrown into water, is converted into the oxide with evolution of sulphuretted hydrogen—

$$Al_2S_3 + 3H_2O = Al_2O_3 + 3H_2S.$$

The compound is decomposed in the same manner by atmospheric moisture, when exposed to the air.

## THALLIUM.

Formula, Tl. Molecular weight = 203.7.

**History.**—Thallium was discovered by Crookes (1861) in the seleniferous deposit from a sulphuric acid manufactory. In the spectroscopic examination of certain residues obtained in the extraction of selenium from this deposit, the presence of an unknown element was manifested, by the appearance of one bright green line. From its characteristic spectrum, the name *thallium* (signifying a green twig) was given to the element.

**Occurrence.**—Thallium is found in small quantities in many varieties of iron pyrites, and when these are employed in the manufacture of sulphuric acid, oxide of thallium collects in the flue dust of the pyrites burners. Thallium also occurs associated with copper, selenium, and silver, in the rare mineral *crookesite.*

**Mode of Formation.**—The metal is obtained by reducing the sulphate, by immersing strips of zinc into the solution. The thallium is deposited upon the zinc, as a spongy or crystalline mass, which is then pressed together, and fused beneath potassium cyanide in a crucible.

**Properties.**—Thallium is a soft heavy metal, resembling lead. It is readily cut with a knife, and leaves a streak when drawn across paper. When preserved out of contact with air, it is a tin-white lustrous metal; but on exposure to the air, it tarnishes upon its surface, with the formation of black thallous oxide. Its specific gravity is 11.8, and it melts at 290°.

When exposed to air and moisture, or when placed in water which is free to absorb atmospheric oxygen, the metal is slowly converted into thallous hydroxide, which is soluble in water, and imparts to the liquid a strong alkaline reaction. The solution absorbs carbon dioxide, with the formation of thallous carbonate. When heated in the air thallium melts, and rapidly oxidises to thallium trioxide, $Tl_2O_3$; heated in oxygen it burns, forming the same oxide. It readily burns when heated in chlorine, producing thallous chloride, TlCl. The metal is soluble in dilute acids.

**Oxides of Thallium.**—Two oxides are known, namely, thallous oxide, $Tl_2O$, and thallic oxide, $Tl_2O_3$.

**Thallous Oxide,** $Tl_2O$, forms as a dark grey film upon the surface of the metal, on exposure to the air. It may also be obtained by heating the hydroxide to 100°. It dissolves in water, forming the hydroxide.

**Thallous Hydroxide** is obtained by the addition of barium hydroxide to a solution of thallous sulphate, the precipitated barium sulphate being removed by filtration—

$$Tl_2SO_4 + Ba(HO)_2 = BaSO_4 + 2TlHO.$$

The solution, on concentration, deposits yellow needle-shaped crystals of $TlHO,H_2O$. Thallous hydroxide is soluble in water, yielding an alkaline solution, which gives a brown stain upon turmeric paper. This stain soon disappears, owing to the destruction of the colouring-matter, and is thereby distinguished from the similar stains produced by sodium and potassium hydroxides.

**Thallic Oxide,** $Tl_2O_3$, is obtained when thallium burns in the air, or when thallium oxyhydroxide, TlO(HO), is heated to 100°. It forms a dark reddish powder, insoluble in water. In warm dilute sulphuric acid it dissolves, forming thallic sulphate—

$$Tl_2O_3 + 3H_2SO_4 = Tl_2(SO_4)_3 + 3H_2O,$$

but with hot concentrated acid oxygen is evolved, and thallous sulphate formed—

$$Tl_2O_3 + H_2SO_4 = Tl_2SO_4 + O_2 + H_2O.$$

At a red heat thallic oxide is converted into thallous oxide with loss of oxygen.

**Thallium Oxyhydroxide,** $TlO(HO)$, is formed by the action of potassium hydroxide upon thallium trichloride—

$$TlCl_3 + 3KHO = 3KCl + H_2O + TlO(HO).$$

**Thallous Chloride,** $TlCl$, is obtained as a white curdy precipitate, when hydrochloric acid is added to a solution of a thallous salt. It is considerably more soluble in hot than in cold water: 100 parts of water at 16° dissolve 0.265 parts; and at 100°, 1.427 parts of thallous chloride.

**Thallic Chloride,** $TlCl_3$, is formed by passing chlorine through water, in which thallous chloride is suspended. The solution so obtained, on evaporation in vacuo, deposits colourless transparent crystals of $TlCl_3,2H_2O$.

When either thallium or thallous chloride is gently heated in a stream of chlorine, a compound is obtained, having the composition $TlCl_3,TlCl$, or $Tl_2Cl_4$. If this be further heated, it loses chlorine, and is converted into a yellow crystalline compound of the composition $TlCl_3,3TlCl$, or $Tl_4Cl_6$, thus—

$$2Tl_2Cl_4 = Cl_2 + Tl_4Cl_6.$$

**Thallous Oxysalts.**—The *sulphate* $Tl_2SO_4$, and *nitrate* $TlNO_3$, are best obtained by dissolving the metal in the respective acids. Both salts are soluble in water.

**Thallous Carbonate,** $Tl_2CO_3$, is prepared by saturating a solution of thallous hydroxide with carbon dioxide. The salt forms long white prismatic (monosymmetric) crystals, which are moderately soluble in water, giving an alkaline solution.

**Thallous Phosphate,** $Tl_3PO_4$, is obtained by precipitation from a thallous solution, by the corresponding potassium phosphate. The monohydrogen phosphate, $HTl_2PO_4$, on being heated to 200°, is converted into pyrophosphate—

$$2HTl_2PO_4 = H_2O + Tl_4P_2O_7,$$

and the dihydrogen salt, on being ignited, yields the metaphosphate—

$$H_2TlPO_4 = H_2O + TlPO_3.$$

**Thallic Oxysalts.**—The chief of these are thallic sulphate,

$Tl_2(SO_4)_3$ ; and thallic nitrate, $Tl(NO_3)_3$. They are obtained by the action of sulphuric acid and nitric acid respectively upon thallic oxide, $Tl_2O_3$. Thallic sulphate forms colourless crystals of the composition $Tl_2(SO_4)_3,7H_2O$. It is decomposed by excess of water, with precipitation of the hydrated oxide ; and when heated, yields thallous sulphate, sulphur trioxide, and oxygen—

$$Tl_2(SO_4)_3 = Tl_2SO_4 + 2SO_3 + O_2.$$

Thallic nitrate is deposited in colourless crystals of $Tl(NO_3)_3,8H_2O$, which are decomposed in the presence of much water.

# CHAPTER IX

## *THE ELEMENTS OF GROUP IV*

| Family A. | | Family B. | |
|---|---|---|---|
| *Titanium*, Ti | 48 | Carbon, C | 11.97 |
| *Zirconium*, Zr | 90.4 | Silicon, Si | 28.3 |
| *Cerium*, Ce | 141.2 | *Germanium*, Ge | 72 |
| *Thorium*, Th | 232 | Tin, Sn | 117.35 |
| | | Lead, Pb | 206.39 |

**Family A** consists of four rare elements.* Titanium, as the oxide $TiO_2$, occurs in the three rare minerals—*rutile*, *brookite*, and *anatase*. The metal is extremely difficult to isolate in a pure state, owing to the fact that it unites directly with nitrogen, forming a nitride.

Zirconium is met with as the silicate $ZrSiO_4$ (or $ZrO_2,SiO_2$) in the mineral *zircon*. Like silicon, it has been obtained in two forms, crystalline and amorphous. The latter variety, when gently heated, burns in the air, while the crystalline variety requires the high temperature of the oxyhydrogen flame for its ignition.

Cerium occurs associated with lanthanum, in the rare minerals *cerite* and *orthite*, and with yttrium and ytterbium in *gadolinite* and *wöhlerite*.

Thorium is found in the extremely rare minerals, *thorite* and *orangeite*, met with in Norway.

**Family B.**—In this family the rare element germanium forms a link between carbon and silicon on the one hand, and tin and lead on the other.

Carbon (the typical element) is essentially non-metallic, and forms an acidic oxide. Silicon approaches more nearly to the metals in its physical properties, but its oxide is still acidic, and no compounds are known in which silicon functions as a basic element. Germanium is both metallic and non-metallic ; its oxide unites with acids; and it also combines with alkaline hydroxides, forming germanates corresponding to silicates. Tin is a still more basic element, forming well-marked salts with acids; but it is also acidic, and with alkalies forms stannates.

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* For descriptions of these rare elements, the student is referred to larger treatises.

Carbon and silicon exhibit a close relationship. They both form allotropes, which correspond in many respects. They both unite with hydrogen, forming the analogous compounds $CH_4$ and $SiH_4$; and with hydrogen and chlorine they form the similarly constituted compounds, chloroform, $CHCl_3$; and silicon chloroform, $SiHCl_3$.

Tin and lead approach more nearly to each other, especially in their physical properties, than to the other members of the family. They both form compounds, in which the metals function both as divalent and tetravalent elements. Although in the case of lead (as often happens with the heaviest metals of a family), the element exhibits much greater readiness to act in the lower state of atomicity. Until quite recently (1893), no compound was known in which an atom of lead is united with four monovalent atoms, although lead ethide, $Pb(C_2H_5)_4$, had been obtained. Now, however, the compound $PbCl_4$ has been produced, corresponding to $SnCl_4$, which it resembles in many respects; and still more recently (1894), the tetrafluoride has been obtained.

Carbon, as usual with the typical elements, stands apart from the other members of the family in many of its attributes. Thus, its oxides are both gaseous: it also forms a vast number of compounds with hydrogen, oxygen, and nitrogen, the study of which constitutes the science of organic chemistry. This element has already been treated in Part II. (page 250).

## SILICON.

Symbol, Si. Atomic weight = 28.3.

**Occurrence.**—Silicon is not known to occur in the uncombined state, although in combination it is the most abundant and widely distributed of all the elements, with the exception of oxygen. In combination with oxygen, as silicon dioxide or *silica*, $SiO_2$, it occurs as *flint*, *sand*, *quartz*, *rock crystal*, and *chalcedony;* while in combination with oxygen and such metals as calcium, magnesium, and aluminium, it occurs in clay and soil, and constitutes a large number of the rocks which make up the earth's crust. Silicon, in combination with oxygen, is also met with in the vegetable kingdom, being absorbed by plants from the soil.

**Modes of Formation.**—(1.) Silicon may be obtained by strongly heating a mixture of potassium silico-fluoride and potassium—

$$K_2SiF_6 + 2K_2 = Si + 6KF.$$

The mass, after cooling, is treated with water, which dissolves the potassium fluoride, leaving the liberated silicon.

(2.) This element may also be prepared by heating sodium in a stream of the vapour of silicon tetrachloride—

$$SiCl_4 + 2Na_2 = Si + 4NaCl.$$

As obtained by either of these methods the silicon is in the form of an amorphous, dark brown powder.

(3.) Silicon is obtained in a crystalline condition, by passing a slow stream of the vapour of silicon tetrachloride over aluminium, previously melted in a current of hydrogen; the volatile aluminium chloride passes on in the stream of gas, and the liberated silicon dissolves in the excess of aluminium—

$$3SiCl_4 + 4Al = 3Si + 2Al_2Cl_6.$$

As the mass cools, silicon is deposited in the form of long, lustrous, needle-shaped crystals.

(4.) The most convenient method for the preparation of crystallised silicon, consists in heating in a crucible a mixture of 3 parts of potassium silico-fluoride, 1 part of sodium, and 4 parts of granulated zinc. The regulus so obtained contains crystallised silicon. It is gently heated, and the excess of zinc drained away, the remainder being removed by treatment with acids.

**Properties.**—**Amorphous Silicon**, as obtained by the reactions Nos. 1 and 2, is a dark brown amorphous powder, having a specific gravity of 2.15. When heated in the air it burns with the formation of silicon dioxide, which, being non-volatile, coats the particles of the element, and protects it from complete oxidation. It burns when heated in a stream of chlorine, with formation of silicon tetrachloride. It is insoluble in water, and in all acids except hydrofluoric acid, in which it dissolves, with the formation of silicofluoric acid and evolution of hydrogen—

$$Si + 6HF = H_2SiF_6 + 2H_2.$$

On boiling with potassium hydroxide, it forms potassium silicate and hydrogen—

$$Si + 2KHO + H_2O = K_2SiO_3 + 2H_2.$$

**Crystallised Silicon.**—As obtained by reactions Nos. 3 and 4, silicon is a brilliant, steely-grey substance, crystallised in needles derived from the rhombic octahedron. The specific gravity of the crystals is 2.34 to 2.49. Crystallised silicon does not burn in oxygen, even when strongly heated: it burns when heated in chlorine, and takes fire spontaneously when brought into fluorine. It is not soluble in any acid except a mixture of nitric and hydrofluoric acids. Crystallised silicon is very hard, being capable of scratching glass. When silicon is exposed to a high temperature, out of contact with air, it becomes denser and harder, and has been obtained in the form of small, steel-grey nodules, showing a crystalline structure, and having a specific gravity as high as 3.0.*

**Silicon Hydride,** $SiH_4$.—This compound is evolved at the negative electrode (along with hydrogen), when dilute sulphuric acid is electrolysed, the electrodes consisting of aluminium containing silicon.

In an impure condition, also mixed with hydrogen, this gas may be obtained by the action of hydrochloric acid upon magnesium silicide—

$$SiMg_2 + 4HCl = 2MgCl_2 + SiH_4.$$

---

* Although silicon in combination is such an abundant element, constituting, as it does, about one-fourth of the total weight of the solid crust of the earth, in the free state it must still be regarded as somewhat of a rarity, and consequently a good deal of uncertainty exists as to its properties. From differences that have been observed in the substance, as obtained by different methods, and from the close analogy that exists between silicon and carbon, it was at one time believed that three allotropes of this element existed, corresponding to those of carbon. Amorphous silicon was considered to represent charcoal. A crystalline substance obtained by Wöhler, by heating potassium silico-fluoride with aluminium, has been regarded as corresponding to graphite, and called *graphitic* silicon; while the octahedral crystals of silicon prepared by reactions 3 and 4 given above (Deville), were thought to be the analogue of diamond; and this substance has, therefore, been called *diamond*, or *adamantoid* silicon. There is considerable doubt as to whether the silicon obtained by all these various methods was sufficiently pure to warrant this classification, and this doubt is not diminished by the recently discovered fact, that silicon unites with carbon, forming a hard crystalline substance, which has received the name *carborundum*.

(Magnesium silicide for this reaction may be prepared by fusing together, in a covered crucible, a mixture of dry magnesium chloride 40 parts, dry sodium chloride 10 parts, sodium silico-fluoride 35 parts, and metallic sodium 20 parts.)

Pure silicon hydride is prepared by acting upon triethyl silico-formate with metallic sodium. The mode of action of the sodium is not known, the ethyl silico-formate breaks up into silicon hydride and ethyl silicate—

$$4SiH(OC_2H_5)_3 = SiH_4 + 3Si(OC_2H_5)_4.$$

**Properties.**—Silicon hydride is a colourless gas. As obtained by the first two methods it inflames spontaneously. The pure gas does not possess this property. Its ignition point, however, is very low, and if the gas be slightly warmed, or if a jet of it be caused to impinge upon an object a few degrees above the ordinary temperature, the gas at once takes fire and burns with a brightly luminous flame: it is also rendered spontaneously inflammable by reduction of pressure, or by admixture with hydrogen. When brought into chlorine the gas takes fire, with formation of silicon chloride and hydrochloric acid.

**Silicon Fluoride,** $SiF_4$.—This compound is formed when silicon is brought into fluorine, the silicon taking fire spontaneously in the gas.

It is prepared by the action of sulphuric acid upon a mixture of powdered fluorspar and sand—

$$2CaF_2 + 2H_2SO_4 + SiO_2 = 2CaSO_4 + 2H_2O + SiF_4.$$

**Properties.**—Silicon fluoride is a colourless, fuming gas. It is not inflammable, and does not support combustion. It is decomposed by water into hydrofluosilicic acid, and silicic acid, hence the gas cannot be collected over water—

$$3SiF_4 + 3H_2O = 2H_2SiF_6 + H_2SiO_3.$$

The silicic acid is precipitated as a gelatinous mass. Each bubble of gas as it comes in contact with the water is at once decomposed, and a little sack-like envelope of silicic acid is formed round it. On filtering the liquid, a solution of hydrofluosilicic acid is obtained. When silicon fluoride is passed over strongly heated silicon, a white powder is obtained, having the composition $Si_2F_6$.

**Silicon Chloride,** $SiCl_4$, is formed when silicon is heated in a stream of chlorine. Under these circumstances the silicon burns in the gas.

It is obtained by heating an intimate mixture of silica and carbon in a stream of chlorine, and passing the products through a cooled tube—

$$SiO_2 + 2C + 2Cl_2 = 2CO + SiCl_4.$$

**Properties.**—Silicon chloride is a colourless liquid, which fumes strongly in moist air, and boils at 58.3°. It is decomposed by water into silicic and hydrochloric acids—

$$SiCl_4 + 4H_2O = Si(HO)_4 + 4HCl,$$

and the silicic acid so formed, passes either entirely or in part into the dibasic acid, thus—

$$Si(HO)_4 = SiO(HO)_2 + H_2O.$$

**Disilicon hexachloride** (also known as silicon trichloride), $Si_2Cl_6$, is formed when the vapour of silicon tetrachloride is passed over strongly heated silicon—

$$3SiCl_4 + Si = 2Si_2Cl_6.$$

It may be prepared by gently heating the corresponding iodine compound, with mercuric chloride—

$$Si_2I_6 + 3HgCl_2 = Si_2Cl_6 + 3HgI_2.$$

**Properties.**—Disilicon hexachloride is a mobile, colourless, fuming liquid, which boils at 147° and crystallises at $-1°$. When the liquid is boiled, and the hot vapour allowed to escape into the air, it spontaneously ignites.

Silicon forms two compounds with bromine and with iodine, corresponding to the chlorides, namely—

$$SiBr_4\,;\ Si_2Br_6\,;\ SiI_4 : Si_2I_6.$$

**Silicon Dioxide,** $SiO_2$, occurs in nature in a more or less pure form in a large number of minerals, some of which have already been alluded to, as natural compounds of silicon. Silicon dioxide in an amorphous form, is met with in the different varieties of *opal*, and in enormous quantities in the deposit known as *kieselguhr*. This substance consists of the remains of extinct diatomaceæ, and is met with in various parts of Germany. In a crystalline condition silica occurs as *quartz* or *rock crystal*, and also in a rarer form as *tridymite*.

**Modes of Formation.**—(1.) Silicon dioxide is formed when amorphous silicon is burnt in air or oxygen.

(2.) It may be prepared by heating silicic acid, which readily parts with water, and leaves pure silicon dioxide as a light white amorphous powder—

$$Si(HO)_4 = SiO_2 + 2H_2O \text{ ; or}$$
$$SiO(HO)_2 = SiO_2 + H_2O.$$

(3.) In minute crystals, silicon dioxide is obtained by strongly heating a solution of an alkaline silicate in a sealed glass tube, whereby a portion of the silica of the glass is dissolved. When this solution is cooled, silicon dioxide is deposited. If the crystallisation takes place above a temperature of 180°, crystals of quartz are obtained; if below this point, it deposits crystals of tridymite, while at ordinary temperatures the silica is deposited in the amorphous condition. Much larger quartz crystals have been obtained, by the prolonged heating to 250°, of a 10 per cent. aqueous solution of silicic acid (obtained by dialysis), in stout sealed glass flasks.

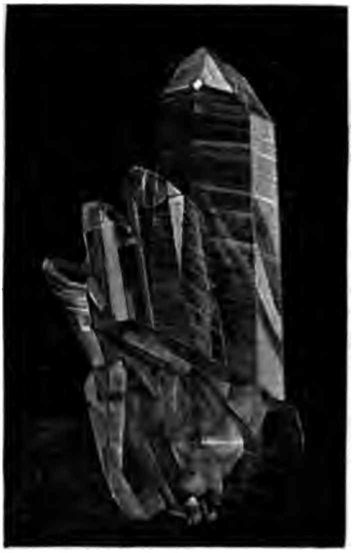

Fig. 141.

**Properties.**—In the crystalline condition as *quartz*, silicon dioxide forms prismatic crystals belonging to the hexagonal system, terminating in hexagonal pyramids. Fig. 141 represents a mass of quartz or rock crystal.

The purest forms of rock crystal are perfectly colourless, having a specific gravity of 2.69, and are sufficiently hard to cut glass. When cut and polished, it exhibits a brilliancy not far inferior to that of the diamond, and is occasionally substituted for this gem.

Quartz is often found coloured by the presence of small quantities of impurities, as in the varieties known as *amethyst quartz* and *smoky quartz*, and in great quantities as *milky quartz*.

The variety of silicon dioxide known as *tridymite*, is found as minute crystals in cavities in certain specimens of trachytic rocks. The crystalline form of tridymite, although belonging to the hexagonal system, is distinct from that of quartz, and the crystals are frequently met with grown together in the manner known as *twin-crystals*.

Amorphous silicon dioxide, as it occurs in nature, is a translucent substance, having a conchoidal or vitreous fracture; its specific gravity is 2.3. As artificially prepared, it is a soft white powder, whose specific gravity is 2.2. At the temperature of the oxy-hydrogen flame, silicon dioxide melts to a transparent glass-like substance, which is capable of being drawn out into fine threads resembling spun glass. These fibres possess many valuable properties, and are employed by physicists in delicate instruments of precision.

Silicon dioxide is insoluble in water, and in all acids with the exception of hydrofluoric acid. It dissolves in alkalies, and the amorphous powder can be dissolved in a boiling solution of sodium carbonate. Many natural hot springs contain silica held in solution as an alkaline silicate, and on exposure to atmospheric carbon dioxide, the silicate is decomposed with the deposition of silica and the reformation of an alkaline carbonate. The enormous quantities of siliceous sinter deposited by geysers at Rotomahama, New Zealand, were formed in this way. When fused with sodium carbonate, silicon dioxide is converted into soluble sodium silicate—

$$SiO_2 + 2Na_2CO_3 = 2CO_2 + Si(NaO)_4.$$

**Silicic Acids.**—Silicon dioxide is capable of forming weak polybasic acids, but from the readiness with which they give up water, it is probable that none have ever been obtained in a state of purity. The compound represented by the formula $Si(HO)_4$ is known as orthosilicic acid, and is tetrabasic. By the loss of one molecule of water, it forms metasilicic acid, $SiO(HO)_2$. When hydrochloric acid is added to a solution of an alkaline silicate, a gelatinous precipitate is obtained, which consists of the dibasic acid $SiO(HO)_2$, or $H_2SiO_3$—

$$SiO(NaO)_2 + 2HCl = SiO(HO)_2 + 2NaCl.$$

If, on the other hand, the solution of alkaline silicate be added cautiously to an excess of hydrochloric acid, the silicic acid remains in solution, and is probably present as orthosilicic acid, $Si(HO)_4$, or $H_4SiO_4$—

$$SiO(NaO)_2 + 2HCl + H_2O = Si(HO)_4 + 2NaCl.$$

The sodium chloride in the solution may be removed by a process of separation known as dialysis. This process, discovered by Graham, is based upon a property belonging to certain classes of substances, of passing when in solution through certain membranes. The mixture is placed in an apparatus resembling a small tambourine (Fig. 142) (made by stretching either parchment, or parchment paper, over a wooden hoop), which is then floated upon water. The sodium chloride passes through the membrane, while the silicic acid remains behind in the dialyser, as a dilute aqueous solution. Substances in solution which are capable of readily diffusing through such a membrane, were termed by Graham *crystalloids;* while others, such as the silicic acid, which either do not pass through, or only do so with difficulty, are known as *colloids.*

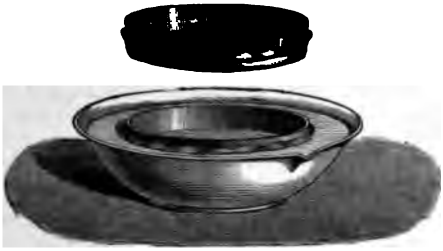

FIG. 142.

This aqueous solution of silicic acid may be concentrated by boiling, and further by evaporation in vacuo over sulphuric acid, until it contains about 21 per cent. of tetrabasic silicic acid, or 14 per cent. of silicon dioxide. In this condition it is a tasteless liquid, having a feeble acid reaction. It cannot be preserved, as on standing it solidifies to a transparent gelatinous mass, which has approximately the composition $H_2SiO_3$.

**Silicates.**—The silicates constitute a large class of important minerals, many of which are of extremely complex composition. Some of the simplest of these silicates are derived from the dibasic and tetrabasic acids already described, while others may be regarded as the salts of a number of hypothetical polybasic silicic acids, derived from metasilicic acid by the gradual elimination of water. Thus, by the withdrawal of one molecule of water from two molecules of metasilicic acid, an acid known as disilicic acid is obtained, having the composition $Si_2O_3(HO)_2$, or $2SiO_2,H_2O$, or $H_2Si_2O_5$—

$$2SiO(HO)_2 = H_2O + Si_2O_3(HO)_2.$$

By the abstraction of one molecule of water from two molecules of orthosilicic acid another disilicic acid is similarly derived—

$$2Si(HO)_4 = H_2O + Si_2O(HO)_6, \text{ or } 2SiO_2,3H_2O, \text{ or } H_6Si_2O_7.$$

By the partial withdrawal of water from three molecules of silicic acid a number of hypothetical trisilicic acids may be derived, such as—

$$3SiO_2,2H_2O \text{ or } H_4Si_3O_8;\ 3SiO_2,5H_2O \text{ or } H_{10}Si_3O_{11};$$
$$3SiO_2,7H_2O \text{ or } H_{14}Si_3O_{13}.$$

Silicates derived from an acid containing one atom of silicon are termed monosilicates; those from acids with two or three atoms of silicon respectively, disilicates and trisilicates.

Thus, the mineral *peridote* is a monosilicate, $Mg_2SiO_4$.

*Serpentine* is a disilicate, $Mg_3Si_2O_7$, and

*Felspar*, or *orthoclase*, is a trisilicate, $Al_2K_2(Si_3O_8)_2$.

## TIN.

Symbol, Sn. Atomic weight = 117.35.

**Occurrence.**—Tin does not occur in nature in the uncombined state.[*] It is met with chiefly as the oxide $SnO_2$ in the mineral *tin-stone* or *cassiterite*,[†] which is found in immense deposits, although in comparatively few localities. It is usually associated with arsenical ores, copper pyrites, wolfram (a tungstate of iron and manganese), and other minerals. Occasionally it is met with in nodules of nearly pure oxide, known as *stream-tin*.

**Mode of Formation.**—Tin is obtained exclusively from *tin-stone:* and the process with ordinary ore consists of three operations, namely—(1) calcining, (2) washing, (3) reducing or smelting. If the ore be nearly pure tin-stone it may be at once smelted.

The finely crushed ore, after being washed from earthy matters, is calcined in a reverberatory furnace. The sulphur and arsenic pass away as sulphur dioxide and arsenious oxide, and are led into condensing flues, where the arsenic deposits and is collected. The iron and copper are oxidised to oxide and sulphate. This calcination is sometimes conducted in the revolving calciner, shown on page 446. The calcined ore is next washed, whereby copper sulphate is dissolved, and the iron oxide and other light matters are removed. The purified ore is then mixed with powdered anthracite, and smelted in a reverberatory furnace—

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[*] Metallic tin has been found in Bolivia, but its origin, whether natural or artificial, is doubtful.

[†] Cassiterides, the ancient name for the British Isles, is derived from the fact that tin-stone was found in large quantities in Devonshire and Cornwall.

$$SnO_2 + 2C = 2CO + Sn.$$

The metal so obtained, is purified by first heating it upon the hearth of a similar furnace, until the more readily fusible tin melts and flows away from the associated alloys; and afterwards by stirring into the molten tin so separated, billets of green wood, which results in the separation of a scum or dross carrying with it the impurities.

**Properties.**—Tin is a bright white metal, which retains its lustre unimpaired in the air. It is sufficiently soft to be cut with a knife, but is harder than lead, although less hard than zinc. At ordinary temperatures it is readily beaten out into leaf (known as tin-foil), and may be drawn into wire; but at temperatures a little below its melting-point (228°) it becomes brittle and may be powdered. Tin may be obtained in the form of crystals, by melting a quantity of the metal in a crucible, and when partially solidified, pouring out the remaining liquid portion. Its crystalline character is also seen by pouring over the surface of a block of cast tin, or a sheet of ordinary tinned iron, a quantity of warm dilute aqua-regia, when the surface of the metal will immediately exhibit a beautiful crystalline appearance.

When a bar of tin is bent, it emits a faint crackling sound, and if quickly bent backwards and forwards two or three times, the metal becomes perceptibly hot at the point of flexure. These phenomena are due to the friction of the crystalline particles. When strongly heated, tin takes fire and burns, forming stannic oxide, $SnO_2$. It is oxidised by both sulphuric and nitric acids; thus, when heated with strong sulphuric acid, stannous sulphate and sulphur dioxide are produced—

$$Sn + 2H_2SO_4 = SnSO_4 + SO_2 + 2H_2O.$$

The strongest nitric acid (specific gravity, 1.5) is without action upon tin. Ordinary concentrated nitric acid (specific gravity, 1.24) attacks it with violence, forming metastannic acid (p. 593), while in cold dilute acid, it slowly dissolves with the production of stannous nitrate—

$$4Sn + 9HNO_3 = 4Sn(NO_3)_2 + 3H_2O + NH_3.$$

The ammonia unites with another portion of nitric acid, forming ammonium nitrate. Strong hydrochloric acid converts it into stannous chloride, with evolution of hydrogen.

Tin is extensively employed in the process of *tinning*, which consists in coating other metals with a thin film of tin, by dipping into a bath of the molten metal. Ordinary tin-plate (or in common parlance, "tin," the material of which articles generally called "tins" are made) is thin sheet-iron which has been thus superficially coated with tin.

**Alloys of Tin.**—Tin enters into the composition of a large number of useful alloys. With lead, tin will mix in all proportions, and many alloys are in use consisting of these two metals. They are all white, and melt at temperatures lower than that of either constituent.

**Pewter** contains 3 parts of tin to 1 part of lead. Common *solder* consists of 1 part tin and 1 part lead, while coarse and fine solder contain half, and twice this proportion of tin respectively. With copper, the most important alloys are the various brasses and bronzes. Britannia metal contains tin 84 parts, antimony 10 parts, copper 4 parts, and bismuth 2 parts. Tin is a constituent also of the so-called *fusible alloys* (see Bismuth, page 461).

**Oxides of Tin.**—Two oxides are definitely known, namely, stannous oxide, $SnO$, and stannic oxide, $SnO_2$. The monoxide is a base, yielding the *stannous salts;* the dioxide is both a basic and an acidic oxide.

**Stannous Oxide,** $SnO$, is obtained by heating stannous oxalate out of contact with air, thus—

$$SnC_2O_4 = SnO + CO_2 + CO.$$

When sodium carbonate and stannous chloride are mixed, carbon dioxide is evolved, and the white hydrated oxide is precipitated, thus—

$$2SnCl_2 + 2Na_2CO_3 + H_2O = 4NaCl + 2CO_2 + 2SnO,H_2O.$$

When this hydrated oxide is boiled with insufficient caustic alkali to dissolve it, the undissolved portion is dehydrated and converted into the black monoxide.

When heated in the air, stannous oxide becomes incandescent, burning to the dioxide. It is soluble in acids, forming stannous salts. The solution of stannous oxide in sodium hydroxide is used by the calico printer, and is known commercially as *sodium stannite*.

**Stannic Oxide,** $SnO_2$ (*tin dioxide*), is the chief ore of tin. It is formed where the metal is burnt in the air, but is most readily prepared by igniting metastannic acid.

It is a white amorphous powder, which changes to yellow and brown on heating, but returns to its original condition on cooling. When strongly heated in a stream of gaseous hydrochloric acid, it may be obtained in small crystals, identical with the natural compound. Stannic oxide is unacted upon by acids or alkalies, but in contact with fused potassium hydroxide it is converted into potassium stannate.

**Stannic Acid,** $H_2SnO_3$, or $SnO_2,H_2O$, is obtained in a hydrated condition, as a white gelatinous precipitate, when calcium carbonate is added to stannic chloride in insufficient quantity for complete precipitation. When the precipitate is dried in vacuo, it has the composition $H_2SnO_3$. The equation representing its formation may be expressed thus—

$$2CaCO_3 + SnCl_4 + H_2O = 2CaCl_2 + 2CO_2 + H_2SnO_3.$$

Stannic acid forms a number of salts, of which sodium and potassium stannates are the most important; the former being extensively employed as a mordant in dyeing, under the name of *preparing salt*. The salts have the composition $Na_2SnO_3,3H_2O$, and $K_2SnO_3,3H_2O$ respectively, and are both soluble in water.

**Metastannic Acid,** $H_{10}Sn_5O_{15}$, is obtained as a white amorphous powder, when tin is acted upon by strong nitric acid; the reaction may be represented thus—

$$5Sn + 20HNO_3 = H_{10}Sn_5O_{15} + 5H_2O + 20NO_2.$$

The composition of the compound depends upon the particular temperature at which it is dried. This acid is sometimes regarded as a polymer of stannic acid, which may be expressed by the formula $5(H_2SnO_3)$; metastannic acid, however, appears to be dibasic, forming salts in which two only of the hydrogen atoms are replaced; its composition may therefore be conveniently expressed thus—

$$H_2SnO_3,4SnO_2,4H_2O, \text{ or } H_2Sn_5O_{11},4H_2O.$$

Potassium and sodium metastannates are the best known salts, their formulæ being—

$$K_2SnO_3,4SnO_2,4H_2O, \text{ and } Na_2SnO_3,4SnO_2,4H_2O.$$

**Stannous Chloride,** $SnCl_2$, is obtained by dissolving tin in hydrochloric acid, and evaporating the solution, when monosymmetric prisms separate out, having the composition $SnCl_2,2H_2O$. When dried in vacuo they become anhydrous. The anhydrous chloride is directly obtained when tin filings and mercuric chloride are heated together—

$$HgCl_2 + Sn = SnCl_2 + Hg.$$

The reduced mercury volatilises and leaves the chloride, which at a higher temperature may be distilled.

Stannous chloride dissolves in a small quantity of water, but with an excess of water, or on exposure to the air, an oxychloride (or basic chloride) is precipitated with simultaneous elimination of hydrochloric acid, thus—

$$2SnCl_2 + 2H_2O = SnCl_2,SnO,H_2O + 2HCl.$$

The composition of this oxychloride may also be expressed by either of the following formulæ—

$$Sn_2OCl_2,H_2O, \text{ or } 2Sn(OH)Cl, \text{ or } 2(SnO,HCl).$$

Stannous chloride is a powerful reducing agent, as it readily combines with either oxygen or chlorine; thus, when added to a solution of mercuric chloride, the latter is first reduced to mercurous chloride, which, on being gently warmed, is reduced to metallic mercury—

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4.$$
$$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4.$$

By the absorption of oxygen, the above oxychloride and stannic chloride are formed, thus—

$$3SnCl_2 + O + H_2O = SnCl_2,SnO,H_2O + SnCl_4.$$

Stannous chloride boils at a temperature about 606°. The density of the vapour only agrees with the formula $SnCl_2$ at temperatures above 900°, at lower temperatures its vapour density approaches more nearly to that required by the formula $Sn_2Cl_4$.

**Stannic Chloride,** $SnCl_4$, is obtained by passing a stream of dry chlorine over melted tin in a glass retort; or by heating a mixture of powdered tin with an excess of mercuric chloride, when the anhydrous chloride distils over as a colourless, mobile, fuming liquid, which boils at 113.9°. It unites with water with evolution of heat, forming hydrated compounds of the composition $SnCl_4,3H_2O$; $SnCl_4,5H_2O$, and $SnCl_4,8H_2O$. The compound containing $5H_2O$ is employed as a mordant, and is commercially known as *oxymuriate of tin.*

Stannic chloride combines with alkaline chlorides forming double chlorides (sometimes called *chloro-stannates*), such as $SnCl_4,2NH_4Cl$, and $SnCl_4,2KCl$.

**Stannous Sulphide,** SnS.—When tinfoil is introduced into sulphur vapour the metal takes fire, and yields a leaden-coloured mass of stannous sulphide.

In the hydrated condition, stannous sulphide is precipitated as a brown powder, when sulphuretted hydrogen is passed through stannous chloride; on drying, this becomes black and anhydrous.

Stannous sulphide dissolves in hot concentrated hydrochloric acid. It is also soluble in alkaline polysulphides, forming sulphostannates, thus—

$$(1)\quad 4SnS + K_2S_5 = K_2SnS_3 + 3SnS_2.$$
$$(2)\quad SnS_2 + K_2S = K_2SnS_3.$$

On the addition of hydrochloric acid to the solution, *stannic* sulphide is precipitated—

$$K_2SnS_3 + 2HCl = 2KCl + H_2S + SnS_2.$$

**Stannic Sulphide,** $SnS_2$.—This compound cannot be formed by heating tin and sulphur alone, as the heat of the reaction is greater than that at which stannic sulphide is resolved into stannous sulphide and sulphur. It is obtained by heating tin amalgam, sulphur and ammonium chloride, in a retort. The action that takes place is a complicated one, various products being volatilised, and stannic sulphide remaining in the retort as a mass of golden yellow scales. Amongst the products expelled during the process are ammonium chloride, sulphur, mercuric chloride, mercuric sulphide, and sulphuretted hydrogen. The ammonium chloride present, probably acts by the formation of ammonium stannous chloride, as an intermediate product, which is then decomposed with the production of stannic sulphide and ammonium stannic chloride, thus—

$$2SnCl_2,2NH_4Cl + 2S = SnS_2 + NH_4Cl + SnCl_4,2NH_4Cl.$$

Stannic sulphide is a golden yellow crystalline substance, which when heated, partially sublimes as such, but is for the most part decomposed into the monosulphide and free sulphur. It is largely used as a pigment known as *mosaic gold*.

## LEAD.

Symbol, Pb. Atomic weight = 206.39.

**Occurrence.**—Lead has been found in small quantities in the uncombined state, probably reduced from its ores by volcanic action.

In combination with sulphur it occurs in enormous quantities in the mineral *galena*, PbS, which is the ore from which the metal is chiefly obtained. Large quantities are also met with as carbonate in the mineral *cerussite*, $PbCO_3$. Other natural compounds are *anglesite*, $PbSO_4$; *lanarkite*, $PbSO_4,PbO$; *matlockite*, $PbCl_2,PbO$; *pyromorphite*, $3Pb_3P_2O_8,PbCl_2$.

**Modes of Formation.**—Lead is very readily reduced from its compounds, and on this account was one of the earliest known metals. It was termed by the Romans *plumbum nigrum*.

Two general processes are made use of for the reduction of lead from its ores:—

In the first method (known as the *reduction process*), the lead sulphide is reduced by double decomposition with lead oxide and sulphate, which are formed by roasting the ore.

In the second (called the *precipitation process*), the sulphide is reduced by metallic iron.

(1.) The galena is introduced into a reverberatory furnace, where it is partially roasted, whereby a portion of the sulphide is oxidised to sulphate and oxide—

$$PbS + 2O_2 = PbSO_4.$$
$$2PbS + 3O_2 = 2PbO + 2SO_2.$$

The temperature is then raised, when the oxide and sulphate react upon a further portion of the sulphide, with the formation of metallic lead and the evolution of sulphur dioxide—

$$PbSO_4 + PbS = 2Pb + 2SO_2.$$
$$2PbO + PbS = 3Pb + SO_2.$$

This method of lead smelting is followed when the ore is fairly free from other metallic sulphides. The reverberatory furnace usually employed (known as the *Flintshire furnace*) has a considerable depression, or well, in the hearth, where the metallic lead collects during the process, and from which it is drawn off into a metal pot.

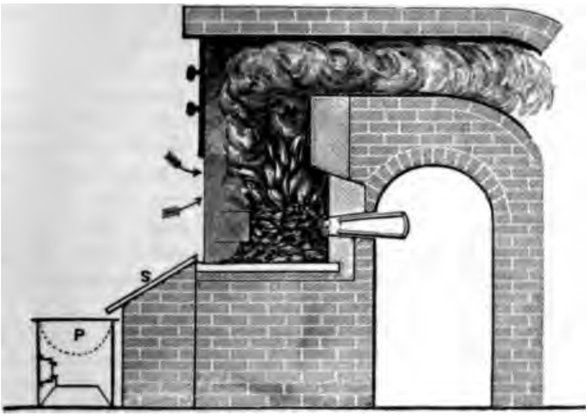

FIG. 143.

The same process is carried out in the North of England, and in Scotland, where a very pure lead ore is employed, upon open shallow hearths (known as the *ore hearth*, or *Scotch hearth*), built under a brickwork hood or chimney in such a manner that the fumes of lead which escape are caused to pass into condensing chambers. Fig. 143 shows such a hearth in section. The fire of peat and coal is urged by a small blast admitted from behind, and the ore is added in small quantities at a time. The reduced metal sinking to the bottom, runs under the fire-bar, and overflows from the shallow hearth down a channel upon an inclined stone surfaces (called the *work-stone*) into an iron pot P, which is gently heated by a small fire to enable the operator to ladle the metal out into moulds.

(2.) This method of lead smelting depends upon the fact, that at a high temperature metallic iron, in contact with lead sulphide, is converted into ferrous sulphide, with separation of lead—

$$PbS + Fe = FeS + Pb.$$

The ores (either in the raw state, or after previous calcination) are smelted in a blast-furnace with coke and either metallic iron, or such materials as will yield iron under the furnace conditions. The sulphide of iron, along with other metallic sulphides, rises to the top of the molten lead as a matt or regulus, while above this a fusible slag collects, consisting chiefly of silicate of iron.

The lead first obtained by any of these processes usually contains antimony, tin, copper, and other metals. These impurities are removed by heating the metal in a shallow, flat-bottomed reverberatory furnace. Most of the admixed metals oxidise before the lead, and collect in the dross which forms upon the surface. This process is known as the *softening of lead.* The silver, however, which is always present, is not removed by this operation, but is extracted by one of the methods for desilverising lead described under silver, page 516.

**Properties.**—Lead is a soft, bluish-white metal, which when freshly cut exhibits a bright metallic lustre. On exposure to the air its bright surface becomes quickly covered with a film of oxide. Lead is sufficiently soft to be scratched with the finger nail, and it leaves a black streak when drawn across paper. It cannot be hammered into foil, or drawn into wire, but may readily be obtained in these forms by rolling and pressing. When a quantity of melted lead is allowed partially to resolidify, and the still liquid portion poured off, the metal is obtained in the form of octahedral crystals belonging to the regular system. Its crystalline nature is also readily seen by submitting a solution of a lead salt to electrolysis, when the metal is deposited upon the negative electrode in beautiful arborescent crystals with a brilliant metallic lustre (Fig. 144). It is deposited in a similar form, known as the *lead tree*, by suspending a strip of zinc in such a solution. The specific gravity of lead is 11.3 ; it melts at 330° to 335°, and becomes covered with a black film of the suboxide, $Pb_2O$ : when more strongly heated it is oxidised to the monoxide, $PbO$.

Lead is rapidly dissolved by nitric acid, but hydrochloric and sulphuric acids are almost without action upon it in the cold. Hot concentrated hydrochloric acid, however, slowly converts it into lead chloride.

Lead is unacted upon by pure water, in the absence of air; but in contact with air, lead hydroxide is formed, which is slightly soluble in water. By the action of atmospheric carbon dioxide upon this solution, a basic carbonate is precipitated, having the composition $2PbCO_3,Pb(HO)_2$. The solvent action of water upon lead is greatly influenced by the presence of various dissolved substances in the water; thus, water containing small quantities of ammoniacal salts, notably the nitrate, dissolves lead much more rapidly, and the same is the case with water charged with carbon dioxide under pressure. In the latter case the action is probably due to the formation of a soluble acid carbonate.

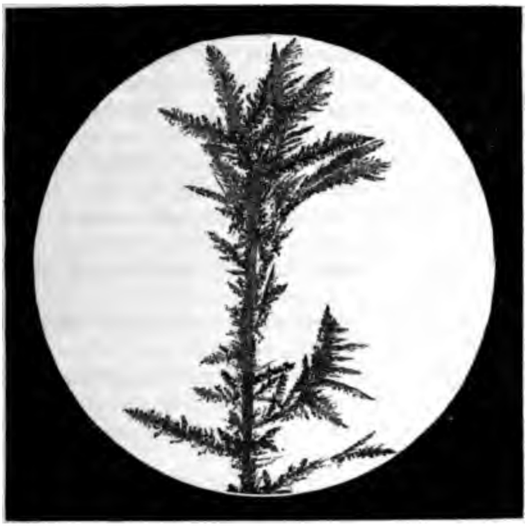

FIG. 144.

Water, on the other hand, containing small quantities of phosphates and carbonates, especially the acid calcium carbonate, are almost entirely without action upon lead. Certain drinking waters (such as the Loch Katrine water), which on account of their purity exert a solvent action upon the lead pipes through which they are conveyed, are rendered incapable of acting upon the lead by being first filtered through chalk or animal charcoal, which enables them to take up sufficient calcium carbonate or phosphate to prevent this action.

On account of the exhaustive methods of desilverisation to which the lead is subjected, commercial lead possesses a degree of purity not found in any other metal as commonly met with; the total amount of foreign metals present in ordinary commercial lead, ranges from 0.1 to 0.006 per cent.

Lead is put to a large number of uses in the arts, on account of the ease with which it can be worked, and its power of resisting the action of water and many acids. In the manufacture of lead pipes advantage is taken of the extreme softness of the metal, and the readiness with which it can be pressed into shape; the lead, in a pasty or semi-molten condition, being merely squeezed, or *squirted*, through a steel die, by hydraulic pressure.

Lead bullets are also made by squeezing the metal into moulds; for as lead contracts on solidification, bullets made by casting always contain a small cavity, which (unless it happens to form exactly at the point of centre of gravity) renders the flight of the bullet untrue.

**Oxides of Lead.**—Five oxides of lead are known, having the composition $Pb_2O$, $PbO$, $Pb_2O_3$, $Pb_3O_4$, $PbO_2$.

**Lead Suboxide** (*plumbous oxide*), $Pb_2O$, is the black compound which is formed when lead is heated to its melting-point. It is obtained by heating plumbic oxalate to about 300° in a glass tube or retort—

$$2PbC_2O_4 = CO + 3CO_2 + Pb_2O.$$

When heated in the air it burns, forming plumbic oxide; in the absence of air it is decomposed into the same oxide and metallic lead, the reactions being—

$$Pb_2O + O = 2PbO.$$
$$Pb_2O = Pb + PbO.$$

In contact with acids it decomposes in the same manner, lead being deposited, and the plumbic oxide dissolving in the acid to form a plumbic salt.

**Plumbic Oxide** (*lead monoxide*, *litharge*, *massicot*), $PbO$, is formed when lead is strongly heated in the air, and is obtained in large quantities in the cupellation of argentiferous lead. It may be obtained by heating lead nitrate or carbonate, and it is produced when any of the other oxides are heated.

Plumbic oxide is a yellowish powder, known commercially as *massicot*, which, when melted and resolidified, is obtained as a crystalline mass, known as *litharge*. Plumbic oxide is very slightly soluble in water, 1 part dissolving in 7000 parts of water: this solution is alkaline, and on exposure to the air absorbs carbon dioxide, forming an insoluble basic carbonate. Plumbic oxide is dissolved by acids, with formation of the salts of lead; it also dissolves in warm potassium, or sodium hydroxide.

This oxide forms two hydrated compounds, having the composition $2PbO,H_2O$ and $3PbO,H_2O$. The former is obtained as a white precipitate when ammonia is added to a solution of lead acetate; the second, by the action of ammonia on basic lead acetate at 25°.

**Lead Sesquioxide,** $Pb_2O_3$, is obtained as an orange-coloured precipitate by adding sodium hypochlorite to a solution of plumbic oxide in potassium hydroxide. Heat decomposes it into oxygen and plumbic oxide. Acids convert it into the monoxide and dioxide, the former dissolving and yielding a salt of lead. This oxide may be regarded as a compound of two oxides, $PbO,PbO_2$.

**Triplumbic Tetroxide** (*red lead*, *minium*), $Pb_3O_4$, is obtained when lead carbonate, or monoxide, is subjected to prolonged heating in contact with air, at a temperature not above 450°. At higher temperatures it again gives up oxygen. It is a scarlet crystalline powder, varying somewhat in colour, according to its mode of preparation. Dilute acids convert it into $PbO_2$ and $2PbO$, the latter oxide dissolving to yield lead salts. With strong hydrochloric acid and sulphuric acid, the molecule of lead dioxide is acted upon with evolution of chlorine and oxygen respectively—

$$Pb_3O_4 + 8HCl = 4H_2O + 3PbCl_2 + Cl_2.$$
$$Pb_3O_4 + 3H_2SO_4 = 3H_2O + 3PbSO_4 + O.$$

Red lead* is employed as a pigment, and also in the manufacture of flint glass.

---

* Commercial red lead varies considerably in composition, and although it has been shown that a definite compound exists, of the composition $Pb_3O_4$ (which may also be expressed by the formula $2PbO,PbO_2$), it is still uncertain whether there are not other compounds consisting of these two oxides united in different proportions.

**Plumbic Peroxide** (*lead dioxide*), $PbO_2$, may be obtained by the action of dilute nitric acid upon red lead—

$$Pb_3O_4 \text{ (or } PbO_2,2PbO) + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O.$$

Or it may be prepared by the action of oxidising agents upon the monoxide. Thus, when chlorine is passed through an alkaline solution, in which the monoxide is suspended, or when bleaching-powder is added to a solution of lead acetate, the dioxide is produced.

The dark brown deposit which forms upon the positive electrode when a solution of a lead salt is electrolysed, also consists of the dioxide.

Plumbic peroxide is a brown or puce-coloured powder. It is a powerful oxidising substance, and when gently rubbed with flowers of sulphur in a warm mortar the mass suddenly inflames. When a stream of sulphur dioxide is passed over the peroxide in a tube, the two compounds unite to form lead sulphate, the mass becoming incandescent. Nitric acid is without action upon it, but hydrochloric and sulphuric acids act upon it in the same manner as upon red lead. When strongly heated, the peroxide gives up oxygen, and is converted into the monoxide.

When plumbic peroxide is boiled with strong aqueous potassium hydroxide it dissolves, and the solution deposits crystals of potassium plumbate, $K_2PbO_3,3H_2O$. This compound corresponds with potassium stannate, $K_2SnO_3,3H_2O$, and its existence shows that lead possesses, although to a very feeble extent, the acidic properties exhibited by the other members of the same family of elements.

**Plumbic Chloride** (*lead dichloride*), $PbCl_2$, is obtained as a white curdy precipitate, when hydrochloric acid, or a soluble chloride, is added to a solution of a lead salt. It is also produced by the action of boiling hydrochloric acid upon lead in the presence of air. It is best prepared by dissolving lead oxide or carbonate in hot hydrochloric acid, when the lead chloride separates out on cooling, in long white, lustrous, needle-shaped crystals belonging to the rhombic system. Lead chloride is soluble in boiling water to the extent of about 4 parts in 100 parts of water. On cooling the solution, the greater part of the salt separates out, and at 0° the liquid contains 0.8 parts in solution. The presence of hydrochloric acid and soluble chlorides diminishes the solubility of lead chloride.

When heated in contact with air, it is converted into an oxychloride, of the composition $Pb_2OCl_2$, or $PbCl_2,PbO$, corresponding with the natural compound *matlockite*. This compound, in the hydrated condition, $Pb_2OCl_2,H_2O$, is prepared on a large scale by the addition of lime-water to a solution of lead chloride, and is employed as a white pigment, known as *Pattinson's white lead.*

*Cassel yellow* is an oxychloride of lead of the composition $PbCl_2,7PbO$, obtained by heating lead oxide and ammonium chloride.

**Lead Tetrachloride** (*lead perchloride*), $PbCl_4$.—When plumbic peroxide is dissolved in cold concentrated hydrochloric acid, a yellow liquid is obtained, which, on warming, yields chlorine, with precipitation of lead dichloride. This liquid contains the tetrachloride of lead in solution.

When lead dichloride is suspended in hydrochloric acid, and chlorine is passed through the mixture, a solution of lead tetrachloride is obtained ; and on the addition of ammonium chloride, ammonium plumbic chloride, $PbCl_4,2NH_4Cl$ (corresponding to ammonium stannic chloride), separates out. When this compound is acted upon with strong sulphuric acid, in the cold, lead tetrachloride separates out as a yellow oily liquid.

Lead tetrachloride is a yellow, highly-refracting, fuming liquid, which decomposes in contact with moisture into lead dichloride and chloride. It may be preserved beneath concentrated sulphuric acid. With small quantities of water, it forms a hydrated compound, but excess of water decomposes it into hydrochloric acid and lead peroxide—

$$PbCl_4 + 2H_2O = PbO_2 + 4HCl.$$

When heated with strong sulphuric acid to about 105°, it suddenly decomposes with explosion.

**Lead Nitrate,** $Pb(NO_3)_2$, is obtained by dissolving litharge in nitric acid. The salt is deposited from the solution in the form of regular octahedral crystals. It is soluble in water to the extent of 50 parts in 100 parts of water, at the ordinary temperature. When heated, it evolves nitrogen peroxide and oxygen, leaving plumbic oxide (page 217).

On boiling an aqueous solution of lead nitrate with lead oxide, the latter dissolves, and the solution on cooling, deposits crystals of a basic nitrate, $Pb(NO_3)HO$ or $Pb(NO_3)_2,PbO,H_2O$. By the addition of ammonia to a solution of lead nitrate, other basic nitrates are obtained, which may be regarded as consisting of compounds of $Pb(NO_3)HO$ with PbO, or of $Pb(NO_3)_2$ with PbO and $H_2O$ in varying proportions.

**Lead Carbonate,** $PbCO_3$, is obtained as a white crystalline powder, by the addition of ammonium sesquicarbonate to a solution of lead nitrate. It occurs in the form of transparent rhombic crystals in the mineral *cerussite*, isomorphous with arragonite. Lead carbonate is almost insoluble in water, but is appreciably dissolved in water charged with carbon dioxide. When sodium or potassium carbonate is added to a solution of lead nitrate, basic carbonates of lead are precipitated, varying in composition with the conditions of temperature. The most important of the basic carbonates is *white lead*, $2PbCO_3,Pb(HO)_2$. This compound is manufactured on a large scale by several processes, for use as a pigment. The oldest process, and that which yields the best product, is known as the *Dutch method*. It depends upon the action of acetic acid upon metallic lead, in the presence of moist air and carbon dioxide. The lead, cast into rough gratings in order to expose a large surface, is placed in earthenware pots, as shown in Fig. 145. A small quantity of dilute acetic acid (in the old Dutch process, *vinegar*) is placed in the pots, and the gratings of lead, which rest upon the shoulder of the pot, are piled one upon the other. These pots are then placed upon a thick bed of spent tan-bark (in the original method, *dung*), upon the floor of a shed, and covered with planks. Upon these another layer of tan-bark is spread, and a second row of pots similarly charged. In this manner the layers of pots are built up to the roof of the shed, and the whole allowed to remain for about three months. Such a stack will contain many tons of lead, and about 65 gallons of dilute acetic acid to the ton of metal. The acid is gradually vaporised by the heat developed by the fermenting tan-bark, which results first in the formation of a basic lead acetate—

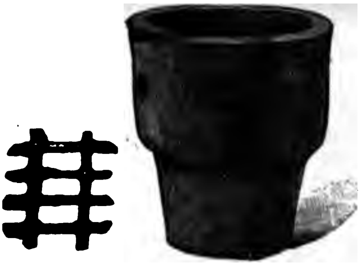

FIG. 145.

$$2H(C_2H_3O_2) + 2Pb + O_2 = Pb(C_2H_3O_2)_2,Pb(HO)_2.$$

This basic acetate is then acted upon by the carbon dioxide evolved during the fermentation, with the production of a mixture of normal lead acetate, and basic lead carbonate, thus—

$$6\{Pb(C_2H_3O_2)_2,Pb(HO)_2\}+2CO_2=3Pb(C_2H_3O_2)_2+2PbCO_3,Pb(HO)_2+2H_2O.$$

And the lead acetate, in the presence of air and moisture, reacts upon a further portion of the metal, regenerating the basic acetate, which is once more decomposed by carbon dioxide—

$$Pb(C_2H_3O_2)_2 + Pb + O + H_2O = 2\{Pb(C_2H_3O_2)_2,Pb(HO)_2\}.$$

In this cycle of reactions, therefore, the acetic acid acts as a carrier, a comparatively small quantity being able to convert an indefinite amount of lead into *white lead.*

White lead is also prepared by passing carbon dioxide into a solution of the basic acetate, obtained by boiling plumbic oxide (litharge) with lead acetate. The product, however, is not so opaque as that obtained by the former method, and is therefore not so valuable as a pigment. (This method is known as the *Clichy*, or Thénard's process.)

*Milner's process* consists in grinding together litharge, sodium chloride, and water, whereby a mixture of an oxychloride of lead and sodium hydroxide is formed—

$$4PbO + 2NaCl + 5H_2O = PbCl_2,3PbO,4H_2O + 2NaHO,$$

and then passing carbon dioxide into the mixture, which converts it into *white lead* and sodium chloride, thus—

$$3[PbCl_2,3PbO,4H_2O] + 6NaHO + 8CO_2 = 6NaCl + 4[2PbCO_3,Pb(HO)_2] + 11H_2O.$$

White lead is a heavy, amorphous powder, whose value as a pigment, or body colour, depends upon its opacity and density. Although this compound labours under the disadvantages of being extremely poisonous, and of becoming blackened by sulphuretted hydrogen, no substitute for it has yet been found which possesses the same "body" or covering power.

**Lead Sulphate,** $PbSO_4$.—The mineral *anglesite*, $PbSO_4$, occurs in the form of rhombic crystals, isomorphous with strontium and barium sulphates. Lead sulphate is obtained as a white powder, by precipitating a lead salt with sulphuric acid, or a soluble sulphate. It is soluble in water only to an extremely slight extent, and still less in dilute sulphuric acid, but strong sulphuric acid dissolves it readily. It also dissolves in potassium hydroxide, and in many ammoniacal salts, notably the acetate, and in sodium thiosulphate.

An acid sulphate, of the composition $PbSO_4,H_2SO_4,H_2O$ is obtained by boiling the normal sulphate with sulphuric acid; and a basic sulphate, $PbSO_4,PbO$, is formed by the action of ammonia upon the normal salt.

**Lead Sulphide,** PbS.—The natural sulphide, *galena*, is found in the form of cubical crystals, possessing very much the colour and the metallic lustre of freshly cut lead. It is artificially formed when lead is heated in sulphur vapour, or when sulphuretted hydrogen is passed through a solution of a lead salt.

When heated in vacuo, or in a stream of an inert gas, lead sulphide melts, and sublimes in the form of small cubes.* When heated with free access of air it is converted into lead sulphate.

Boiling dilute nitric acid converts lead sulphide into the nitrate, with separation of sulphur; but strong nitric acid oxidises it into lead sulphate. It is decomposed by hot concentrated hydrochloric acid, with evolution of sulphuretted hydrogen.

When sulphuretted hydrogen is passed into a solution of lead chloride, the precipitate which forms is first yellow, then reddish-brown, and finally black; the yellow and red precipitates are compounds of lead chloride and lead sulphide, termed sulphochlorides, having the composition, $PbS,PbCl_2$, and $3PbS,PbCl_2$.

The compounds of lead are powerful poisons, and when continuously taken into the system in small quantities, they act as cumulative poisons. Painters and others who constantly handle white lead, are liable to suffer from chronic lead poisoning.

---

* From the readiness with which lead sulphide volatilises when heated in a stream of sulphur dioxide, Hannay concludes (*Proc. Chem. Soc.*, May 1894), that the two substances unite to form a volatile compound, $PbS,SO_2$, or $PbS_2O_2$, which when its temperature falls, again breaks up into lead sulphide and sulphur dioxide. When sulphur dioxide is generated in intimate contact with galena, as when a stream of air is passed through the molten substance, it is observed that one half of the lead is reduced, and one half volatilises with the gas, according to the equation $2PbS + O_2 = Pb + PbS,SO_2$. No definite proof, however, has yet been adduced as to the existence of this volatile compound.

# CHAPTER X

## *ELEMENTS OF GROUP V. (FAMILY A.)*

***Vanadium***, $V = 51.1$ ; ***Niobium***, $Nb = 93.7$ ; ***Tantalum***, $Ta = 182$.

THE three rare metals comprising this family are closely related to each other, and also to the elements of family B of the same group, namely, the nitrogen and phosphorus series.

Vanadium occurs in a few rare minerals, as *vanadite*, $3Pb_3(VO_4)_2,PbCl_2$ (the vanadium analogue of pyromorphite); *pucherite*, $BiVO_4$; *mottramite*, $(PbCu)_3(VO_4)_2,2(PbCu)(HO)_2$. Small quantities also occur in certain iron ores, the vanadium ultimately finding its way into the Bessemer slag, in which it has been found concentrated to the extent of 1.5 per cent.

Metallic vanadium was first isolated by Roscoe (1867), although its existence was previously discovered by Del Rio (1801). The metal is extremely difficult to obtain, as at a red heat it combines with oxygen with great readiness, yielding the pentoxide $V_2O_5$, and also with nitrogen, forming the nitride VN. The element is prepared by heating the dichloride in a stream of perfectly pure hydrogen—

$$VCl_2 + H_2 = 2HCl + V.$$

Vanadium is unacted upon by air at ordinary temperatures, but when heated burns brilliantly to the pentoxide.

Niobium and tantalum are found associated together in the rare mineral *tantalite* or *columbite*. The first to be discovered was tantalum (Hatchett, 1801), and was originally named *columbium;* and the name niobium (from Niobe, the daughter of Tantalus) was given to the allied element, by Rose (1846). Niobium is obtained by heating the trichloride, $NbCl_3$, in a stream of hydrogen.

Vanadium forms five oxides, corresponding to the oxides of nitrogen, while three oxides of niobium and two of tantalum are known :—

| | | | | |
|---|---|---|---|---|
| $V_2O$ ; | $V_2O_2$(or VO) ; | $V_2O_3$ ; | $V_2O_4$(or $VO_2$) ; | $V_2O_5$. |
| — ; | NbO ; | — ; | $NbO_2$ ; | $Nb_2O_5$. |
| — ; | — ; | — ; | $TaO_2$ ; | $Ta_2O_5$. |

The pentoxides are obtained when the metals are burned in air or oxygen. They give rise respectively to vanadates, niobates, and tantalates, corresponding to nitrates and metaphosphates, thus—

Sodium nitrate, $NaNO_3$.
Sodium metaphosphate, $NaPO_3$.
Sodium metavanadate, $NaVO_3$.
Sodium metaniobate, $NaNbO_3$.
Sodium metatantalate, $NaTaO_3$.

The closer relation of these elements to phosphorus than to nitrogen, is seen in the formation of salts derived from ortho- and pyro-acids, corresponding to orthophosphates and pyrophosphates. The naturally occurring vanadium compounds above mentioned are vanadates derived from the hypothetical orthovanadic acid, $H_3VO_4$. Both metavanadic acid, $HVO_3$, and pyrovanadic acid, $H_4V_2O_7$, have been obtained. Unlike the phosphorus compounds, the metavanadates are the most stable of the three classes of salts, and the orthovanadates the least stable. The most important of these salts is the ammonium metavanadate, $NH_4VO_3$, which is prepared by dissolving the pentoxide in ammonia. This salt is insoluble in ammonium chloride, and use is made of this property in the preparation of vanadium compounds from the mineral *mottramite*. When ammonium metavanadate is ignited, vanadium pentoxide is obtained—

$$2NH_4VO_3 = V_2O_5 + 2NH_3 + H_2O.$$

Vanadium acts also as a feeble base. Thus, when the tetroxide, or hypovanadic oxide, is dissolved in sulphuric acid, hypovanadic sulphate, $V_2O_2(SO_4)_2$, is formed. The solution of this salt possesses a rich blue colour.

Vanadium forms three chlorides, having the composition—

$$VCl_2 \text{ (or } V_2Cl_4); \; VCl_3 \text{ (or } V_2Cl_6); \; VCl_4.$$

Niobium gives a trichloride, $NbCl_3$, and pentachloride, $NbCl_5$, while only the pentachloride of tantalum is known, $TaCl_5$.

Vanadium forms a number of compounds with oxygen and chlorine. Thus, when vanadium tetrachloride is acted upon by water, it yields hypovanadic chloride, $V_2O_4Cl_2$, which dissolves in the water, giving a blue solution.

Vanadium oxychloride, or vanadyl trichloride, $VOCl_3$, corresponds to phosphorus oxychloride, $POCl_3$. From vanadyl trichloride, by treatment with zinc, vanadyl dichloride is obtained, $VOCl_2$, and by the action of hydrogen at a high temperature upon this, both vanadyl monochloride, VOCl, and divanadyl-monochloride, $V_2O_2Cl$, are formed.

# CHAPTER XI

## *ELEMENTS OF GROUP VI. (FAMILY A.)*

| | | | |
|---|---|---|---|
| ium, Cr | 52 | *Tungsten*, W | 184 |
| *enum*, Mo | 95.9 | *Uranium*, U | 239.8 |

### CHROMIUM.

Symbol, Cr. Molecular weight = 52.

**urrence.**—Chromium does not occur in nature in the un- ined state. In combination with oxygen and associated ron, it is met with in considerable quantities in the mineral *e iron ore*, or *chrómite*, $Cr_2O_3,FeO$. This ore is the chief e of chromium compounds. Other natural compounds are *site*, $PbCrO_4$, and *chrome-ochre*, $Cr_2O_3$. Traces of chromium resent in various minerals, such as the emerald and green ntine, and impart to them their green colour.

**des of Formation.**—Although chromium compounds are factured for industrial purposes, the element itself has re- l no technical application.

vas obtained by Wöhler, by the reduction of fused chromium de with metallic zinc, beneath a layer of fused sodium and sium chlorides. The regulus, or alloy of zinc and chromium, hen treated with dilute nitric acid, whereby the zinc was ved, and the chromium was obtained in the form of a er. Chromium may also be obtained as bright metallic , by the electrolysis of a solution of chromous chloride ining chromic oxide. The metal may be prepared by the tion of the oxide, $Cr_2O_3$, by means of carbon, at a high rature; or by heating the oxide with metallic aluminium.

**perties.**—Chromium is a hard, steel-grey metal, which is xidised in dry air. When heated in the oxyhydrogen flame ns brilliantly. It dissolves in hydrochloric acid with evolu- f hydrogen. The metal is not magnetic. The presence of minute quantities of chromium in steel, imparts to the latter great hardness and tenacity.

**Oxides of Chromium.**—Two oxides of chromium are definitely known, namely—

| | |
|---|---|
| Chromium sesquioxide (*chromic oxide*) . . | $Cr_2O_3$. |
| Chromium trioxide (*chromium anhydride*) . . | $CrO_3$. |

The first is a basic, and the second an acidic oxide. Besides these two compounds, a hydrated oxide, derived from the unknown chromous oxide, also exists, having the composition $CrO,H_2O$, or $Cr(HO)_2$. It is obtained as a yellowish precipitate by adding potassium hydroxide to a solution of chromium dichloride (chromous chloride), with the exclusion of air. It rapidly absorbs oxygen, turning dark brown. When heated out of contact with air it is converted into the sesquioxide, with evolution of hydrogen—

$$2CrO,H_2O = Cr_2O_3 + H_2O + H_2.$$

Other compounds of chromium and oxygen are described, whose composition, however, is not definitely established; thus, the product obtained as a brown powder, either by the partial reduction of the trioxide, or the oxidation of the sesquioxide, is regarded by some chemists as chromium dioxide, $CrO_2$, and by others as chromium chromate, $Cr_2O_3,CrO_3$. It is readily obtained by passing nitric oxide into a solution of potassium dichromate.

**Chromium Sesquioxide,** $Cr_2O_3$, is obtained as a grey-green powder, when either the hydroxide, or the trioxide, or ammonium dichromate is ignited (see page 206).

When the vapour of chromyl dichloride, $CrO_2Cl_2$, is passed through a red-hot tube, chromic oxide is deposited in the form of dark-green hexagonal crystals. Chromic oxide which has been strongly ignited, is nearly soluble in acids. It is used under the name of *chrome green* as a pigment, and for giving a green colour to glass.

**Chromic Hydroxides.**—Chromic oxide yields a number of hydrated compounds. When ammonia is added to a solution of chromic chloride, or other chromic salt, free from alkali, a light-blue compound is precipitated, which, when dried over sulphuric acid, has the composition $Cr_2(HO)_6,4H_2O$ (or $Cr_2O_3,7H_2O$). When this is dried in vacuo, it loses $3H_2O$, and becomes $Cr_2(HO)_6,H_2O$ (or $Cr_2O_3,4H_2O$); and on being heated at 200°, it again parts with $3H_2O$, and has the composition $Cr_2O_3,H_2O$.

When potassium dichromate and boric acid are heated to dull redness, and the mass treated with water, a rich green residue is obtained, having the composition $Cr_2O_3,2H_2O$. This compound, known as *Guignet's green*, is employed as a pigment.

The first two of these compounds, which may be looked upon as consisting of the hydroxide $Cr_2(HO)_6$ in a hydrated condition, namely, $Cr_2(HO)_6,4H_2O$ and $Cr_2(HO)_6,H_2O$, are readily soluble in acids, yielding the chromic salts.

**Chromium Trioxide** (*chromic anhydride*), $CrO_3$.—When strong sulphuric acid is added to a cold saturated solution of potassium dichromate, the trioxide separates out in long, red, needle-shaped crystals—

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + H_2O + 2CrO_3.$$

The liquid is decanted from the crystals, which are drained upon porous tiles, and the adhering sulphuric acid and potassium sulphate washed away by strong nitric acid. The crystals are finally heated upon a sand-bath, whereby the nitric acid is evaporated.

Chromium trioxide dissolves in water to the extent of 62 parts in 100 parts of water at 26°. It melts at a temperature about 192°. At 250° it begins to give off oxygen, and is ultimately converted into the sesquioxide—

$$2CrO_3 = Cr_2O_3 + 3O.$$

Chromium trioxide is a powerful oxidising agent, and in contact with most organic substances it is reduced. In the preparation of the compound, therefore, the liquid cannot be filtered through paper in the usual way. Warm alcohol dropped upon the trioxide at once takes fire, while in a more diluted condition it is oxidised to acetic acid; and the reduction of the chromium sesquioxide is made evident by the change of colour of the liquid, from red or yellow, to olive green.

Gaseous ammonia reduces the trioxide to the sesquioxide, with formation of water and nitrogen—

$$2NH_3 + 2CrO_3 = Cr_2O_3 + N_2 + 3H_2O,$$

the reaction being accompanied with the evolution of so much heat that the chromic oxide produced becomes incandescent.

When hydrogen peroxide is added to a dilute solution of chromium trioxide, or to a dilute solution of potassium dichromate, acidified with sulphuric acid, a deep indigo-blue solution is obtained. This blue compound is believed to be *perchromic acid*, but its composition has not been definitely established. It may be regarded as a compound of chromium trioxide, $CrO_3$, with hydrogen peroxide, $H_2O_2$, in undetermined proportions.

In aqueous solution, the blue colour quickly disappears, oxygen being eliminated. The compound is soluble in ether; and, therefore, when the aqueous solution is shaken up with that liquid, a deep blue ethereal solution rises to the top. In this solution the compound is more stable, but when evaporated it evolves oxygen, leaving chromium trioxide. It is decomposed by alkalies, forming alkaline chromates, with evolution of oxygen. The formation of this compound constitutes a delicate test for either chromium trioxide or hydrogen peroxide (see Hydrogen Peroxide, page 203).

**Chromous Compounds.**—These correspond to chromous hydrate, $Cr(HO)_2$, in which the chromium functions as a divalent element. Comparatively few of these salts are known.

**Chromous Chloride**, $CrCl_2$, is formed when the metal dissolves in hydrochloric acid. It is prepared in the anhydrous state by gently heating chromic chloride in a current of pure hydrogen. It is a white crystalline compound, soluble in water to a blue solution, which rapidly absorbs oxygen.

**Chromous Sulphate**, $CrSO_4,7H_2O$, is obtained by dissolving chromous acetate in dilute sulphuric acid. It is deposited from the solution in blue crystals, isomorphous with ferrous sulphate, $FeSO_4,7H_2O$.

**Chromic Compounds.**—These are derived from chromic oxide, the oxide acting as a base.

**Chromic Chloride**, $CrCl_3$, or $Cr_2Cl_6$, is prepared by strongly heating a mixture of chromic oxide, $Cr_2O_3$, and carbon, in a stream of dry chlorine. The chromic chloride sublimes in the form of scales, having a reddish-pink colour. The molecular weight of chromic chloride is 158.6, showing that in the vaporous state its molecules have the formula $CrCl_3$.

It is nearly insoluble in water, but readily dissolves in water containing minute traces of chromous chloride, forming a green solution. The same solution is obtained by dissolving hydrated chromic hydroxide, $Cr_2(HO)_6,4H_2O$, in hydrochloric acid, and if this solution be slowly evaporated, very soluble green crystals separate out having the composition $Cr_2Cl_6,12H_2O$. If strongly heated in the air, this compound gives off water and hydrochloric acid, leaving chromic oxide, $Cr_2O_3$; but when heated to 250°, in either gaseous hydrochloric acid or chlorine, it is converted into the pink anhydrous chromic chloride, which redissolves in water to the green solution. If heated strongly and sublimed, the compound obtained is nearly insoluble in water.

**Chromic Sulphate,** $Cr_2(SO_4)_3$, is obtained by dissolving chromium hydroxide in concentrated sulphuric acid, when a green solution is formed, which on standing changes to blue, and slowly deposits violet-blue crystals. The salt may be purified by dissolving in cold water and precipitating with alcohol. If insufficient alcohol be added to cause immediate precipitation, the salt slowly deposits from the dilute spirit in blue octahedrons, belonging to the regular system.

A cold aqueous solution, which has a violet colour, becomes green when boiled.

Chromic sulphate forms double salts with the sulphates of the alkalies, which belong to the alums.

**Potassium Chromium Alum** (*chrome alum*), $K_2SO_4, Cr_2(SO_4)_3, 24H_2O$.—This double sulphate is formed when solutions of potassium and chromium sulphates are mixed together in molecular proportions. It is most conveniently prepared, by the addition of the requisite amount of sulphuric acid to an aqueous solution of potassium dichromate, and reducing the chromic oxide by passing sulphur dioxide through the liquid—

$$\begin{aligned} &(1)\quad K_2Cr_2O_7 + H_2SO_4 = 2CrO_3 + H_2O + K_2SO_4. \\ &(2)\quad 2CrO_3 + 3SO_2 = Cr_2(SO_4)_3. \end{aligned}$$

The resulting solution, containing the two sulphates in molecular proportions, deposits crystals of the double sulphate, in the form of dark plum-coloured octahedrons (Fig. 140, B, p. 573), which appear red by transmitted light.

Chrome alum dissolves in water, yielding a plum-coloured solution, which on boiling turns green, but on long standing returns to its original colour.

Sodium chromium alum is more soluble, and ammonium chromium alum is less soluble, than the potassium salt.

**Chromites.**—Chromic oxide acts also as a weak base, and combines with other oxides, forming compounds resembling the aluminates. When potassium hydroxide is added to a solution of a chromic salt, the green hydrated oxide which is precipitated contains alkali which cannot be removed by hot water; this is present in the form of potassium chromite. The best known chromites are zinc chromite, $Cr_2O_3,ZnO$; manganous chromite, $Cr_2O_3,MnO$, and ferrous chromite, $Cr_2O_3,FeO$; the latter occurs naturally as chrome iron ore.

**Chromates.**—When chromium trioxide is dissolved in water, the solution is believed to contain chromic acid, $H_2CrO_4$; when the solution is evaporated, however, the trioxide alone is left. (Red crystals have been obtained, by cooling a hot saturated solution of the trioxide, which have been regarded as the acid.)

**Potassium Chromate**, $K_2CrO_4$, is prepared by adding potassium hydroxide to a solution of the dichromate—

$$K_2Cr_2O_7 + 2KHO = 2K_2CrO_4 + H_2O.$$

On evaporation, the *yellow chromate of potash* separates out, in rhombic crystals, isomorphous with potassium sulphate. It is soluble in water at the ordinary temperature to the extent of 60 parts in 100 parts of water, forming a yellow solution having an alkaline reaction.

**Potassium Dichromate**, $K_2Cr_2O_7$, is manufactured from chrome iron ore by roasting the finely crushed ore with potassium carbonate and lime in a reverberatory furnace; the mass being frequently raked over to expose fresh portions to the oxidising action of the flames. In this way a mixture of calcium and potassium chromates is produced—

$$2Cr_2O_3,FeO+3K_2CO_3+CaO+7O = CaCrO_4+3K_2CrO_4+Fe_2O_3+3CO_2.$$

The yellow mass, when cold, is broken up and lixiviated with a hot solution of potassium sulphate, which by double decomposition with the calcium chromate, forms potassium chromate and precipitates calcium sulphate. The solution after settling, is treated with the requisite quantity of sulphuric acid to convert the chromate into the dichromate, thus—

$$2K_2CrO_4 + H_2SO_4 = K_2SO_4 + H_2O + K_2Cr_2O_7.$$

The dichromate being much less soluble than the normal chromate, a large proportion of it at once deposits as the solution cools; and the mother liquor containing potassium sulphate is used again to lixiviate a fresh quantity of the roasted mixture.

Potassium dichromate forms large red prisms or tables, belonging to the asymmetric (triclinic) system. It is soluble in water at the ordinary temperature to the extent of 10 parts in 100 parts of water, yielding an acid solution, which is extremely poisonous. When a film of gelatine is impregnated with potassium dichromate and exposed to light, a reduction of the chromium to chromic oxide takes place, and at the same time the gelatine is rendered insoluble. This property is utilised in photographic processes.*

Potassium dichromate is also known under the misnomer *bichromate of potash*, which would suggest that the salt was in reality hydrogen potassium chromate, corresponding to bisulphate of potash, $HKSO_4$. Such a chromium compound does not exist. The dichromates correspond to the disulphates (or pyrosulphates), see page 396.

**Potassium Trichromate**, $K_2Cr_3O_{10}$ (or $K_2CrO_4,2CrO_3$), and **Potassium Tetrachromate**, $K_2Cr_4O_{13}$ (or $K_2CrO_4,3CrO_3$), are also known.

**Lead Chromate**, $PbCrO_4$, is found as the mineral *crocoisite*. It is produced by precipitation from a lead salt, with either potassium chromate or dichromate. It forms a bright yellow powder, known as *chrome-yellow*, and is employed as a pigment. It melts without decomposition, and resolidifies on cooling to a brown crystalline solid. At higher temperatures it gives off oxygen, and is converted into chromic oxide and a basic lead chromate. When heated with organic compounds, the latter are completely oxidised; lead chromate is therefore employed in organic analyses.

When lead chromate is digested with sodium hydroxide, or with normal potassium chromate, a basic lead chromate is obtained as a rich red powder—

$$2PbCrO_4 + 2NaHO = Na_2CrO_4 + H_2O + Pb_2CrO_5.$$

This compound is known as *chrome-red*.

**Chromyl Chloride**, $CrO_2Cl_2$.—This compound is prepared by distilling a mixture of potassium dichromate and sodium chloride with strong sulphuric acid. Chromyl chloride is a deep red, mobile, strongly fuming liquid. It is decomposed by water into hydrochloric acid and chromium trioxide, and acts as a powerful oxidising substance. When dropped upon phosphorus it explodes. When heated in sealed tubes it is converted into trichromyl chloride with loss of chlorine, $(CrO_2)_3Cl_2$.

Chromyl chloride may be regarded as being derived from chromic acid, $CrO_2(HO)_2$ (*unknown*), by the complete substitution of (HO) by Cl. The intermediate compound, chloro-chromic acid $CrO_2(HO)Cl$ is also unknown, although its salts have been prepared; thus, by the gentle action of hydrochloric acid upon potassium dichromate, potassium chloro-chromate is obtained as a red crystalline salt—

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* Abney, "Treatise on Photography."

$$K_2Cr_2O_7 + 2HCl = 2CrO_2(KO)Cl + H_2O.$$

### Molybdenum, Mo = 95.9 ; Tungsten, W = 184 ; Uranium, U = 239.8.

These three somewhat rare elements are closely related to chromium.

*Molybdenum* occurs in the mineral *molybdenite*, $MoS_2$, (which strongly resembles graphite in appearance), and more rarely as *molybdenum ochre*, $MoO_3$, and *wulfenite*, $PbMoO_4$.

*Tungsten* is found chiefly in *wolfram*, $2FeWO_4,3MnWO_4$ (occurring in the Cornish tin mines); more rarely as *scheelinite*, $PbWO_4$, and *wolfram ochre*, $WO_3$.

*Uranium* occurs as an oxide, $UO_2,2UO_3$, in *pitchblende* (a considerable quantity of which, associated with other uranium compounds, has recently been discovered at St. Stephens, Cornwall).

Molybdenum is obtained by the action of hydrogen upon the heated oxide or chloride; uranium, by the action of sodium upon the chloride; while tungsten has been obtained by both methods. In their specific gravities, tungsten and uranium exhibit a marked difference from chromium and molybdenum; thus, Cr, sp. gr. = 6; Mo, sp. gr. = 8.6; while W, sp. gr. = 19.1; U, sp. gr. = 18.7.

Molybdenum and uranium form a large number of oxides, some of which are regarded as definite oxides, while others are looked upon as combinations of two oxides. Only two oxides of tungsten are known. The composition of these compounds is as follows—

| | | | |
|---|---|---|---|
| $MoO$ | — | — | |
| $Mo_2O_3$ | — | — | |
| $MoO_2$ | $WO_2$ | $UO_2$ | $U_2O_5 = UO_2,UO_3$. |
| $MoO_3$ | $WO_3$ | $UO_3$ | $U_3O_8 = UO_2,2UO_3$. |
| — | — | $UO_4$. | |

The trioxide of each metal is an acid oxide; uranium trioxide, however, is both acidic and basic. They are insoluble in water, but by the action of alkalies they yield molybdates, tungstates, and uranates. Molybdates and tungstates, derived from the acids $H_2MoO_4,2H_2O$, and $H_2WO_4,2H_2O$ (corresponding to chromic acid), are known. And all three oxides yield salts corresponding to potassium dichromate, thus—

| Sodium Dimolybdate. | Sodium Ditungstate. | Sodium Diuranate. |
|---|---|---|
| $Na_2Mo_2O_7$ | $Na_2W_2O_7$ | $Na_2U_2O_7$. |

Molybdic and tungstic acids also form numerous polymolybdates and polytungstates, by the absorption of varying quantities of the trioxide into the molecule of the normal salt (see Chromates, page 615). And in the case of tungsten, the compound, metatungstic acid, $H_2W_4O_{13}.7H_2O$, is known.

Uranium dioxide and trioxide are both basic oxides, the former yielding the unstable *uranous* salts, such as uranous sulphate, $U(SO_4)_2$; and the latter producing the *uranyl* salts, of which the sulphate $(UO_2)SO_4$ and $(UO_2)(NO_3)_2$, are well known.

Uranium peroxide, $UO_4$, is an acid oxide, which yields per-uranates.

Both molybdic and tungstic acids form complex compounds with phosphoric acid, known as phospho-molybdic and phospho-tungstic acids: thus, when a nitric acid solution of ammonium molybdate $(NH_4)_2MoO_4$, is added in excess to a solution of orthophosphoric acid, or an orthophosphate, a canary yellow crystalline precipitate of ammonium phospho-molybdate $2(NH_4)_3PO_4.22MoO_3.12H_2O$ is obtained (see page 437). It is soluble in alkalies and in excess of phosphoric acid, but insoluble in dilute mineral acids. When this compound is dissolved in *aqua-regia*, the solution deposits yellow crystals of phospho-molybdic acid, $2H_3PO_4.22MoO_3$.

Compounds with chlorine having the following composition are known—

| | | |
|---|---|---|
| $MoCl_2$ | $WCl_2$ | — |
| $MoCl_3$ or $Mo_2Cl_6$ | — | — |
| $MoCl_4$ | $WCl_4$ | $UCl_4$. |
| $MoCl_5$ | $WCl_5$ | $UCl_5$. |
| — | $WCl_6$ | — |

## C[redacted] XII

## *GROUP [redacted] MILY A.)*

### [redacted]E.

Symbol, Mn. Molecula[redacted] weight = 54.8.

**Occurrence.**—This element is never found in nature in the free state. It is widely distributed in combination with oxygen, as *pyrolusite*, $MnO_2$; *braunite*, $Mn_2O_3$; and *hausmannite*, $Mn_3O_4$. Also as a hydrated oxide in *manganite*, $Mn_2O_3,H_2O$. It is met with also as carbonate in *manganese spar*, $MnCO_3$; and as sulphide in *manganese blende*, MnS.

**Modes of Formation.**—Manganese may be obtained by the reduction of the oxide by means of carbon, at a very high temperature. The product, however, contains carbon. In a purer state it may be prepared by the reduction of fused anhydrous manganous chloride, by means of metallic magnesium, or by reducing the oxide with aluminium at a high temperature.

**Properties.**—Manganese is a hard, steel-grey, brittle metal. It rapidly oxidises on exposure to moist air, and is readily dissolved by dilute sulphuric or hydrochloric acid, with evolution of hydrogen.

**Oxides of Manganese.**—The four most important of these are—

| | |
|---|---|
| Manganous oxide (*manganese monoxide* . . | MnO. |
| Red manganese oxide (*hausmannite*) . . | $Mn_3O_4$. |
| Manganic oxide (*manganese sesquioxide*) . . | $Mn_2O_3$. |
| Manganese dioxide (*pyrolusite*) . . . . | $MnO_2$. |

The monoxide and sesquioxide are basic, giving rise to manganous and manganic salts respectively. The oxide, $Mn_3O_4$, is also basic, but yields with acids both manganous and manganic salts. Manganeses dioxide, or peroxide, $MnO_2$, gives manganous salts, with elimination of available oxygen. It also combines with certain more basic oxides, forming unstable compounds known as *manganites*.

Manganese trioxide, $MnO_3$, and hept-oxide, $Mn_2O_7$, have also been obtained. They are both acid oxides, giving rise respectively to the *manganates* and *permanganates*.

**Manganous Oxide,** $MnO$, is obtained by heating any of the higher oxides in a stream of hydrogen ; or by igniting a mixture of manganous chloride, sodium carbonate, and ammonium chloride. It is a light green powder, which, if prepared at a low temperature, oxidises in the air. When perfectly air-free solutions of potassium hydroxide and a manganous salt are mixed, with exclusion of air, hydrated manganous oxide, or manganous hydroxide, $Mn(HO)_2$, is obtained as a white precipitate, which rapidly oxidises on exposure to air.

**Red Manganese Oxide** (*mangano-manganic oxide*), $Mn_3O_4$, is the most stable of the oxides of manganese, being formed when both the higher or lower oxides are strongly heated. Thus, in the preparation of oxygen by heating the dioxide, this compound remains (page 162). With cold sulphuric acid, it yields a mixture of manganous and manganic sulphates ; but when heated with dilute acid, manganous sulphate and dioxide are formed—

$$Mn_3O_4 + 2H_2SO_4 = 2MnSO_4 + MnO_2 + 2H_2O.$$

**Manganic Oxide** (*manganese sesquioxide*), $Mn_2O_3$, occurs native as *braunite*, and in the hydrated condition as *manganite*, $Mn_2O_3,H_2O$. The hydrated oxide is formed by the spontaneous oxidation of manganous hydroxide, and when gently heated it yields the oxide. Both the oxide and the hydrate, on treatment with warm nitric acid, yield manganous nitrate and manganese dioxide.

**Manganese Dioxide,** $MnO_2$, is the most important of the manganese ores. It may be obtained by the cautious ignition of manganous nitrate—

$$Mn(NO_3)_2 = N_2O_4 + MnO_2.$$

Manganese dioxide is a hard black solid, which conducts electricity, and is strongly electro-negative to metals. On this account it is employed in certain forms of voltaic battery. When heated it loses oxygen, and forms first the sesquioxide, and finally $Mn_3O_4$. Manganese dioxide dissolves in cold concentrated hydrochloric acid, forming a dark brown solution, which is believed to contain the compound $Mn_2Cl_6$. On warming, it evolves chlorine, and leaves manganous chloride, $MnCl_2$.

**Manganites.**—Manganese dioxide combines with certain metallic oxides, forming unstable compound oxides. Thus with lime it forms $CaO,MnO_2$; $CaO,2MnO_2$, and $CaO,5MnO_2$. These compounds are produced in the *Weldon recovery process* (page 321).

## MANGANOUS SALTS.

**Manganous Chloride,** $MnCl_2$, is the only chloride of this metal that has been isolated. It is obtained by dissolving any of the oxides, or the carbonate, in hydrochloric acid; and on evaporation, is deposited as pink crystals of $MnCl_2,4H_2O$. The anhydrous salt is prepared by heating the crystals in a stream of hydrochloric acid. Manganese chloride forms double salts, with chlorides of the alkalies, the ammonium salt $MnCl_2,2NH_4Cl,H_2O$ being the best known.

**Manganous Sulphate,** $MnSO_4$, is prepared by strongly heating a pasty mixture of the dioxide and strong sulphuric acid. The iron present is thereby converted into ferric oxide, and on treating the calcined mass with water, manganous sulphate dissolves. The solution on evaporation, deposits, at ordinary temperatures, large pink crystals of $MnSO_4,5H_2O$ (isomorphous with copper sulphate). Below 6° rhombic crystals are formed (also pink) of the composition $MnSO_4,7H_2O$ (isomorphous with ferrous sulphate).

When these salts are heated to 200°, or when their solutions are boiled, the anhydrous salt is formed. With sulphates of the alkalies, manganous sulphate forms double salts, as potassium manganous sulphate, $K_2SO_4,MnSO_4,6H_2O$; and with aluminium sulphate it yields a *pseudo-alum* (see page 574), $MnSO_4,Al_2(SO_4)_3$, $24H_2O$.

## MANGANIC SALTS.

**Manganic Chloride** is obtained as a dark brown solution when the dioxide is dissolved in cold hydrochloric acid. It has never been isolated, and is believed to have the composition $Mn_2Cl_6$.

**Manganic Sulphate,** $Mn_2(SO_4)_3$, is obtained as a green deliquescent powder, by the action of sulphuric acid upon the precipitated peroxide. On exposure to the air, the deliquesced mass becomes muddy, by the precipitation of hydrated manganic oxide, thus—

$$Mn_2(SO_4)_3 + 4H_2O = 3H_2SO_4 + Mn_2O_3,H_2O.$$

On the addition of potassium sulphate to a solution of manganic sulphate in dilute sulphuric acid, potassium manganese alum is obtained, $K_2SO_4,Mn_2(SO_4)_3,24H_2O$, which deposits in violet regular octahedra. In the presence of much water the salt is decomposed, and deposits the hydrated manganic oxide.

### MANGANATES.

These salts are derived from the hypothetical manganic acid, $H_2MnO_4$. The oxide corresponding to this acid is known, viz., $MnO_3$. It is an unstable compound, obtained as a reddish amorphous mass, by adding a solution of potassium permanganate in sulphuric acid to dry sodium carbonate.

The manganates of the alkalies are obtained by fusing manganese dioxide with potassium or sodium hydroxide. If air be excluded, the following reaction takes place—

$$3MnO_2 + 2KHO = K_2MnO_4 + Mn_2O_3 + H_2O.$$

In the presence of air or oxygen, or by the addition of potassium nitrate or chlorate, more of the manganese is converted into manganate. The fused mass has a dark green colour, and dissolves in a small quantity of cold water to a deep green solution, which is only stable in the presence of free alkali.

When a solution of potassium manganate is largely diluted, or gently warmed, it changes from green to pink, owing to the conversion of the manganate into permanganate, thus—

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KHO.$$

The same change takes place when carbon dioxide is passed through the solution.

### PERMANGANATES.

These salts are derived from permanganic acid, $HMnO_4$. When potassium permanganate is cautiously added to cold strong sulphuric acid, green oily drops of the unstable manganese heptoxide (or *permanganic anhydride*) are obtained, $Mn_2O_7$. This compound dissolves in a small quantity of water to a purple solution, which contains the unstable acid $Mn_2O_7,H_2O$, or $H_2Mn_2O_8 = 2HMnO_4$. The solution evolves oxygen and deposits manganese dioxide.

**Potassium Permanganate,** $KMnO_4$, is the most important salt of this class. It is prepared by fusing the dioxide with potassium hydroxide and potassium chlorate, dissolving the manganate so obtained in water, and passing carbon dioxide through the solution. The filtered solution, on evaporation, deposits dark purple rhombic prisms, which appear deep red by transmitted light. Potassium permanganate is isomorphous with potassium perchlorate, $KClO_4$: it dissolves in water, forming a rich purple solution. When boiled with strong caustic alkalies it loses oxygen and forms the green potassium manganate—

$$2KMnO_4 + 2KHO = 2K_2MnO_4 + H_2O + O.$$

It readily gives up oxygen to oxidisable and organic compounds, and on this account is used both as a laboratory oxidising agent, and as a disinfectant. The crude sodium salt is largely employed, under the name of *Condy's Disinfecting Fluid*, for this purpose. When solid potassium permanganate is heated to 240° it evolves oxygen, and forms potassium manganate and manganese dioxide—

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2.$$

# CHAPTER XIII

## *THE TRANSITIONAL ELEMENTS OF THE FIRST LONG PERIOD*

**Iron, Fe = 55.88. Cobalt, Co = 58.6.** Nickel, Ni = 58.6.

**These** three elements belonging to Group VIII. (see classification, page 102) stand in a different relation to each other than the members of the other seven groups.

Iron, cobalt, and nickel belong to the same *period*, being the transitional elements falling between the first and second series of the first long period. They are related, on the one hand, through iron, to the preceding metals manganese and chromium (*see such compounds as ferrates*, *manganates*, *chromates*): while, on the other hand, through nickel, they approach the metal copper, which is the next following in the period.

Iron, cobalt, and nickel are closely related elements; in nature they are usually associated together. They are all attracted by the magnet, and are nearly white, hard, and difficultly fusible metals. In their chemical habits, however, they exhibit a gradual transition in their properties. Thus, iron forms two basic oxides, yielding two series of stable salts, viz., *ferrous* and *ferric*. Cobalt also has two basic oxides, but the basicity of the sesquioxide is very feeble, and cobalt*ic* salts (except double salts) are unstable, and are only known in solution. Nickel only forms one basic oxide, and yields only one series of salts corresponding to the ferrous salts: the sesquioxide of nickel behaving with acids as a peroxide.

### IRON.

Symbol, Fe. Molecular weight = 55.88.

**Occurrence.**—Iron is one of the most abundant and widely distributed elements. It occurs in the uncombined state in small particles disseminated through certain basalts, and also in meteoric stone containing from 20 to 25 per cent of coal.

Iron is also found in combination with sulphur,
$FeS_2$, and with iron and copper in copper pyrites,
these compounds are not employed in the metallurg

**Modes of Formation.**—Iron is readily reduced
pounds. Thus, if ferric oxide, or oxalate, be gentl
stream of hydrogen, the metal is obtained as a
which spontaneously oxidises with incandescence
into the air. On the industrial scale the reduction
means of coke and limestone. The ore is first cal
water and carbon dioxide are expelled, and any sul
are oxidised, with the expulsion of sulphur dioxide.
cess also, the ore is rendered more porous. The
then smelted in a blast-furnace, with limestone and
shows in section a modern blast-furnace. The char
at the top by means of the cup and cone arrangemen
the furnace, and a powerful hot-blast is forced th
placed round the base of the furnace. The furnace g
by the side pipe at the top, and are utilised for heati

The chemical reactions which take place in a bla
many and complex, and differ in different parts o
In the main, the following are the changes which
atmospheric oxygen of the hot-blast, on coming i
the carbon, forms carbon monoxide (at the hig

stone is converted into carbon dioxide and lime. The reduced spongy metal, as it passes down through the hotter regions of the furnace, begins to take up carbon. It is probable that carbon monoxide first combines with the reduced iron, forming iron carbonyl (see page 246), which at a higher temperature is decomposed, with the precipitation of finely divided carbon within the pores of the mass. More and more carbon is taken up by the iron

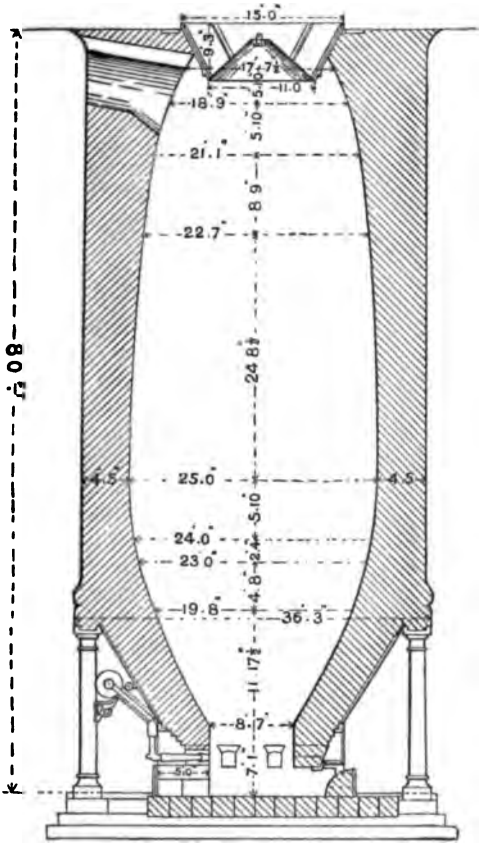

FIG. 146.

as it descends, until it passes from a pasty condition to a state of complete fusion, when it collects upon the bottom, or hearth, of the furnace. In passing through the hottest regions, the lime combines with the siliceous materials originally present in the ore, to form a fusible slag, beneath which the molten iron collects. Other reactions which go on in various regions of the furnace, are the reduction of sulphur compounds, and of phosphates and silicates, with the absorption into the iron of a certain amount of sulphur, phosphorus, and silicon. The precise nature of the changes suffered by the gases in the various regions of the furnace, is still obscure. The cyanogen formed by the direct union of atmospheric nitrogen with carbon, and also the hydrocarbons present, doubtless undergo a chemical change in contact with the heated iron, and probably aid in its carburisation. The molten iron is drawn off at intervals from a tap-hole into moulds, and is known as *cast iron* or *pig iron*. The slag as it accumulates, overflows in a regular stream through an opening known as the *slag hole*. When such a furnace is in full blast, fresh charges of materials are introduced at regular intervals, and the process continues uninterruptedly for years. The metal obtained from the blast-furnace is far from pure iron, but contains varying quantities of carbon, silicon, phosphorus, sulphur, and manganese.

The carbon may be present either in combination with iron as a carbide, or distributed throughout the metal as fine particles of graphite, or in both of these forms. *White cast iron* contains its carbon in the combined form, while *grey cast iron* owes it grey colour to the presence of minute crystals of graphite disseminated throughout the metal. When grey cast iron is dissolved in hydrochloric acid, the graphite remains behind as a black powder; but on similarly treating iron containing *combined carbon*, the carbon unites with the hydrogen, forming various hydrocarbons, which impart to the escaping gas a characteristic and unpleasant smell. Average cast iron contains from 90 to 95 per cent. of iron, and 3 to 5 per cent. of carbon. *Spiegel* is a variety of white cast iron containing 3.5 to 6 per cent. of carbon, and from 5 to 20 per cent. of manganese. With more than 20 per cent. of manganese, the metal is termed *ferro-manganese*.

**Purification.**—The properties of iron are greatly modified by the presence of various impurities, especially carbon, and for different purposes for which iron is used, metal of different degrees of purity is required. The purest form of ordinary commercial iron is known as *wrought iron*, while *steel* is intermediate between this and *cast iron*.

The process by which cast iron is converted into wrought iron, is termed *puddling;* and the method is called either *dry* puddling or *pig-boiling*, depending upon whether the cast iron is subjected to a preliminary refining or not. The chemical reactions in both cases are the same, and consist in the oxidation of the impurities; the carbon being expelled as carbon dioxide, while the oxides of silicon, phosphorus, and manganese pass into the slag. The method of *pig-boiling* is almost exclusively adopted.

The cast iron is melted in a reverberatory furnace, the working bottom of which, as well as the lining (or *fettling*), consists of a layer of ferric oxide. The decarburisation of the iron is mainly effected by means of the oxide of iron derived from the fettling; and for some time the molten mass appears to boil, owing to the escape of carbon monoxide. As the impurities are oxidised and removed, the mass becomes pasty (owing to the fact that the melting-point of pure iron is much higher than that of cast iron), and is then worked up into lumps, or *blooms*, which are ultimately removed and placed under a steam hammer, whereby admixed slag is squeezed out, and the metal is welded into a solid mass.

Wrought iron contains from 0.06 to 0.15 per cent. of carbon.

Steel may be produced either from wrought iron, by adding carbon, or from cast iron by removing that impurity. Formerly steel was exclusively obtained by the first method, by what is known as the *cementation process*. This simply consists in heating the bars of iron, buried in broken charcoal, for several days to a red heat. The precise nature of the chemical change which results in the carburisation of the iron, is not definitely established. In all probability, the carbon is conveyed into the body of the metal (which is not even heated to the softening point) by the intervention of iron carbonyl; the carbon monoxide being formed by the union of the carbon with the air retained within the layer of charcoal. At the conclusion of the operation, the iron presents a blistered appearance, and on this account is termed *blister-steel*.

At the present time, steel is mostly produced by the *Bessemer process*, which consists in oxidising the impurities present in cast iron, by blowing through the molten metal a blast of air. This operation is performed in a large pear-shaped vessel, known as a *converter*, which is mounted on trunnions, and through the bottom of which a powerful air blast can be admitted. The converter is d into a horizontal position, and a quantity of molten cast iron un in. The air blast is then started and the converter immedi- swung back into a vertical position. In the course of a very time the whole of the impurities are burnt away, and the at which the operation is complete is sharply marked, by the en disappearance of the flame from the open mouth of the verter. The converter is once more swung into a horizontal sition, and the blast is stopped. The exact quantity of molten iegel is then added, to supply the carbon required to convert the re charge into steel, and the blast is turned on for a few ents in order to thoroughly mix the materials, after which the ents are poured out into the casting ladle.

e comparative purity of the three forms of iron will be seen the three following typical examples :—

| | Cast Iron. | Steel. | Wrought Iron. |
|---|---|---|---|
| Carbon . . | 3.81 | 0.65 | 0.10 |
| Silicon . . | 1.68 | 0.07 | 0.05 |
| Phosphorus | 0.70 | 0.03 | 0.15 |
| Sulphur . . | 0.60 | 0.02 | 0.05 |
| Manganese | 0.41 | 0.40 | 0.07 |
| | 7.20 | 1.17 | 0.42 |
| Iron . . | 92.80 | 98.83 | 99.58 |
| | 100.00 | 100.00 | 100.00 |

**Properties.**—Pure iron is a white lustrous metal, capable of taking a high polish. Its specific gravity is 7.84 to 8.139. It is more difficultly fusible and more malleable than wrought iron, but at a red heat it becomes soft and can be welded. The physical properties usually associated with iron, are in reality those of iron containing varying amounts of impurities: thus, pure iron when rendered magnetic, quickly loses this property, whereas steel retains its magnetism at ordinary temperatures, losing it, however, when heated. Pure iron, when heated and suddenly cooled, does not take a *temper*, while steel when so treated becomes extremely hard and brittle.

Iron is unacted upon by dry air, at ordinary temperatures, but in moist air, especially in the presence of carbon dioxide, it becomes coated with rust, and the process which is slow to begin, proceeds rapidly when a film of oxide has been once formed. Iron decomposes water readily at a red heat; in the finely divided state, the metal decomposes water at 100°. Dilute hydrochloric and sulphuric acids rapidly dissolve iron with evolution of hydrogen. Dilute nitric acid dissolves it, forming ferrous nitrate and ammonium nitrate; with stronger nitric acid, ferric nitrate and oxides of nitrogen are formed.

Concentrated nitric acid (specific gravity 1.45) is without solvent action upon iron. A strip of iron which has been immersed in such strong acid, is unacted upon when afterwards dipped into the more dilute acid, and is also incapable of precipitating metallic copper from a solution of copper sulphate. Iron in this condition is said to be *passive.* Other oxidising agents, as chromic acid, or hydrogen peroxide, are capable of bringing about the same result. It is believed that this condition is due to the formation of a film of the oxide $Fe_3O_4$ upon the surface.

Finely divided iron takes fire spontaneously in chlorine; and when gently warmed in sulphur dioxide it combines with that gas with incandescence. It absorbs carbon monoxide with formation of iron carbonyl, $Fe(CO)_5$. When heated in ammonia it forms a nitride, $F_5N_2$.

**Oxides of Iron.**—Three oxides of iron are known, namely :—

| | |
|---|---|
| Ferrous oxide (*iron monoxide*) | $FeO$. |
| Ferric oxide (*iron sesquioxide*) | $Fe_2O_3$. |
| Ferroso-ferric oxide (*magnetic oxide*) | $Fe_3O_4$, or $Fe_2O_3,FeO$. |

The two first are basic oxides, giving rise respectively to ferrous and ferric salts: the third yields both ferrous and ferric salts.

Ferric oxide combines with certain more basic oxides, forming compounds analogous to $Fe_2O_3,FeO$; such as $Fe_2O_3,CaO$, $Fe_2O_3ZnO$. These are known as *ferrites*.

**Ferrous Oxide** (*protoxide of iron*), $FeO$, is formed as an intermediate product during the reduction of ferric oxide by hydrogen, or carbon monoxide; but it is difficult to obtain it free from either the higher oxide, or the metal. It is also formed when ferrous oxalate is heated out of contact with air. It is a black powder, which oxidises in the air, and which dissolves in acids yielding ferrous salts.

**Ferrous Hydroxide,** $Fe(HO)_2$, or $FeO,H_2O$, is obtained as a white precipitate, when potassium hydroxide is added to a solution of a ferrous salt with entire exclusion of air. In the presence of air it is green. It readily absorbs oxygen and passes into ferric oxide.

**Ferric Oxide** (*sesquioxide of iron*), $Fe_2O_3$, occurs in brilliant black crystals belonging to the hexagonal system, in *specular iron ore*. It is obtained as a red amorphous powder by heating hydrated ferric oxide, ferrous sulphate, or ferrous carbonate. In a crystalline condition it may be produced by carefully heating a mixture of ferrous sulphate and common salt, or by heating the amorphous oxide in gaseous hydrochloric acid. The natural compound, and also the artificial substance after strong ignition, is only slowly dissolved by acids. Ferric oxide is extremely hygroscopic. When strongly heated it is partially converted into $Fe_3O_4$. The amorphous substance, obtained by distilling ferrous sulphate for the manufacture of Nordhausen sulphuric acid, is employed as a red pigment, and a polishing powder, under the name of *rouge*.

**Ferric Hydroxide,** or **Hydrated Ferric Oxide,** $Fe_2(HO)_6$, or $Fe_2O_3,3H_2O$.—When an excess of ammonia is added to a solution of ferric chloride, and the voluminous brown precipitate is dried at a moderate temperature, it has the composition $Fe_2O_3,3H_2O$. On exposure to various temperatures, or by precipitation under various conditions, hydrated oxides of the composition $Fe_2O_3, 2H_2O$; $Fe_2O_3,H_2O$, and others, have been obtained; and several of these compounds occur in nature. Ordinary rust of iron has the composition $2Fe_2O_3,3H_2O$, or $Fe_2O_3,Fe_2(HO)_6$.

The monohydrate $Fe_2O_3,H_2O$ has been obtained as a soluble modification, by heating an acetic acid solution of precipitated ferric hydroxide to 100° in sealed vessels. On the addition of sulphuric acid, a brown precipitate is obtained, having the composition $Fe_2O_3,H_2O$, which is insoluble in acids, but soluble in water. The solution gives no reaction with potassium ferrocyanide. Another soluble hydroxide is produced by dissolving the ordinary precipitated hydroxide in ferric chloride, and subjecting the solution to dialysis. This solution is employed in medicine under the name of *dialysed iron*.

**Ferroso-ferric Oxide,** $Fe_3O_4$, occurs native as *magnetite* and *magnetic oxide of iron;* the magnetic variety being known also as *loadstone*. When iron is heated in the air, the black film which forms (the so-called *iron-scale*, or *hammer-scale*) consists of the oxide $Fe_3O_4$, with more or less ferric oxide, $Fe_2O_3$, upon the outer surface. It is also produced when steam or carbon dioxide is passed over heated iron, with evolution of hydrogen and carbon monoxide respectively, these reactions being the reverse of those by which oxides of iron are reduced by hydrogen or carbon monoxide.

**Ferrates.**—These compounds correspond to the manganates, but neither the acid $FeH_2O_4$ nor the oxide $FeO_3$ are known. Potassium ferrate, $K_2FeO_4$, is formed when chlorine is passed through a solution of potassium hydroxide in which ferric hydroxide is suspended.

### FERROUS SALTS.

**Ferrous Chloride,** $FeCl_2$.—The anhydrous compound is obtained by heating iron wire in gaseous hydrochloric acid, when the salt sublimes in the form of white deliquescent crystals. In aqueous solution, it is obtained when iron is dissolved in hydrochloric acid, and is deposited in pale blue-green crystals of $FeCl_2,4H_2O$.

When heated in the air it is converted into ferric oxide and chloride, the latter volatilising—

$$6FeCl_2 + 3O = Fe_2O_3 + 2FeCl_3.$$

When volatilised in an atmosphere of hydrochloric acid, its vapour density at high temperatures corresponds to the formula $FeCl_2$; at lower temperatures it lies between the values required for $FeCl_2$ and $Fe_2Cl_4$.

When strongly heated in a current of steam it is decomposed as follows—

$$3FeCl_2 + 4H_2O = Fe_3O_4 + H_2 + 6HCl.$$

**Ferrous Sulphate** (*green vitriol*), $FeSO_4,7H_2O$, is obtained when iron is dissolved in sulphuric acid. It is prepared on a large scale by exposing heaps of iron pyrites, $FeS_2$, to the action of air and moisture. The liquor which drains away contains ferrous sulphate and sulphuric acid, and the latter is converted into ferrous sulphate by the introduction of scrap iron.

Ferrous sulphate forms pale green monosymmetric crystals, which effloresce on exposure to the air. They are soluble in water to the extent of 70 parts in 100 parts of water at 15°, and 370 parts in 100 parts at 90°. At 100° the crystals lose $6H_2O$, being converted into $FeSO_4,H_2O$.

If a crystal of zinc sulphate be thrown into a supersaturated solution of ferrous sulphate, the iron salt is deposited in rhombic prisms (isomorphous with zinc sulphate). On the other hand, if a crystal of copper sulphate be added, asymmetric (triclinic) crystals of $FeSO_4,5H_2O$ (isomorphous with copper sulphate) are formed.

Ferrous sulphate forms double salts with the sulphates of the alkalies. Thus, when mixed with ammonium sulphate in the requisite proportions, ammonium ferrous sulphate, $FeSO_4,(NH_4)_2SO_4,6H_2O$, is obtained. This salt is less readily oxidised on exposure to air than ferrous sulphate itself.

Ferrous salts give, with potassium ferrocyanide ($K_4Fe(CN)_6$, or $4KCN,Fe(CN)_2$), a white precipitate of potassium ferrous ferrocyanide ($FeK_2Fe(CN)_6$, or $2KCN,2Fe(CN)_2$). The precipitate is quickly oxidised, and becomes blue. With potassium ferricyanide ($K_3Fe(CN)_6$, or $3KCN,Fe(CN)_3$), ferrous salts yield a blue precipitate of ferrous ferricyanide (*Turnbull's blue*) ($Fe_3\{Fe(CN)_6\}_2$, or $3Fe(CN)_2,2Fe(CN)_3$), thus—

$$3FeSO_4 + 2K_3Fe(CN)_6 = Fe_3\{Fe(CN)_6\}_2 + 3K_2SO_4.$$

### FERRIC SALTS.

**Ferric Chloride**, $FeCl_3$, is prepared in the anhydrous state by passing dry chlorine over heated iron wire. In solution it may be obtained by dissolving iron in aqua regia; or ferric oxide in hydrochloric acid. The anhydrous salt forms nearly black crystals, appearing deep red by transmitted light. It readily volatilises, and at temperatures above 700° the density of its vapour corresponds to the formula $FeCl_3$, while at lower temperatures its density agrees more nearly with the formula $Fe_2Cl_6$.

Ferric chloride is extremely deliquescent, and readily dissolves in water. When the solution is slowly evaporated, yellow crystals are deposited, having the composition $Fe_2Cl_6,12H_2O$ (or $FeCl_3,6H_2O$). When a dilute solution of ferric chloride is boiled, it decomposes, forming either an insoluble oxychloride, or a soluble hydroxide and free hydrochloric acid (depending upon the strength of the solution).

**Ferric Sulphate**, $Fe_2(SO_4)_3$, is prepared by the addition of sulphuric and nitric acids to a solution of ferrous sulphate—

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 2NO + 4H_2O + 3Fe_2(SO_4)_3.$$

The brown solution, on evaporation, leaves the anhydrous salt as a white mass. When the requisite quantity of potassium sulphate is dissolved in a strong solution of ferric sulphate at 0°, the double potassium iron sulphate (iron alum), $K_2SO_4,Fe_2(SO_4)_3,24H_2O$, separates out in the form of violet octahedrons.

Ferric salts give, with potassium ferrocyanide ($K_4Fe(CN)_6$, or

$4KCN,Fe(CN)_2)$, a dark blue precipitate of ferric ferrocyanide (*Prussian blue*) ($4Fe(CN)_3,3Fe(CN)_2$) or $Fe_4\{Fe(CN)_6\}_3$—

$$4FeCl_3 + 3K_4Fe(CN)_6 = Fe_4\{Fe(C_6N)_6\}_3 + 12KCl.$$

With potassium ferricyanide ferric salts give no precipitate.

### SULPHIDES OF IRON.

**Ferrous Sulphide,** $FeS$.—When a white-hot bar of wrought iron is dipped into melted sulphur, the elements unite; and the readily fusible monosulphide of iron falls to the bottom. It may be prepared by throwing into a red hot crucible a mixture of iron filings and sulphur. So obtained, it is a dark, yellowish-grey, metallic-looking mass. When heated out of contact with air, it does not part with sulphur, but in the presence of air is converted into ferric oxide and sulphur dioxide. Ferrous sulphide is precipitated from either ferrous or ferric solutions, by alkaline sulphides, as a black amorphous powder, which in the moist state is quickly oxidised by the air. Dilute sulphuric acid, or hydrochloric acid, decomposes ferrous sulphide, with evolution of sulphuretted hydrogen.

**Iron Sesquisulphide,** $Fe_2S_3$, is formed when equal weights of iron and sulphur are heated to a moderate temperature. (It cannot be obtained by precipitation from a ferric salt, as the product so formed consists of ferrous sulphide and sulphur—

$$Fe_2Cl_6 + 3(NH_4)_2S = 6NH_4Cl + 2FeS + S.)$$

It is a yellow, metallic-looking solid, which is decomposed by dilute hydrochloric acid, yielding sulphuretted hydrogen.

**Ferric Disulphide,** $FeS_2$, occurs in nature in large quantities as *iron pyrites*, sometimes in the massive condition, and at others in the form of brass-yellow cubical crystals. In many cases the native compound bears the impression, or assumes the shape, of various organised forms, such as wood, ammonites, &c., the mineral having been formed by the reducing action of the organic matter, upon ferrous sulphate in solution. Ferric disulphide is also found in the form of brass-like, rhombic crystals, in *radiated pyrites*.

The compound may be prepared by heating to a low red heat a mixture of ferrous sulphide and sulphur.

Ferric disulphide is unacted upon by dilute acids; hot concentrated hydrochloric acid decomposes it, with liberation of sulphur and sulphuretted hydrogen. When heated in hydrogen, sulphur is evolved (which partly combines with the hydrogen), and ferrous sulphide remains. When heated in the air, ferric oxide and sulphur dioxide are formed.

**Ferroso-ferric Sulphide** (*magnetic pyrites*), $Fe_3S_4$, occurs in the form of hexagonal crystals. Like the corresponding oxide, this compound is attracted by the magnet, and is itself sometimes magnetic.

## COBALT.

Symbol, Co. Molecular weight = 58.6.

**Occurrence.**—With the exception of small quantities present in meteoric iron, cobalt is not found uncombined in nature. Its chief natural compounds, which are only sparsely distributed, are *speiss-cobalt*, or *smaltine*, $CoAs_2$; *cobalt glance*, CoAsS, in both of which the cobalt is partially replaced by nickel and iron; and *cobalt-bloom*, $Co_3(AsO_4)_2,8H_2O$.

**Modes of Formation.**—Cobalt is obtained by reducing the oxide, or the chloride, in a stream of hydrogen, or by strongly heating cobalt oxalate in a closed crucible.

**Properties.**—Cobalt is an almost white, hard metal, which, when polished, resembles nickel, but is slightly bluer. It is malleable, and when heated is very ductile. Like both iron and nickel, it is attracted by the magnet; but unlike these, it retains this property, even at a red heat. In the massive form, cobalt is unacted upon by the air; but the finely-powdered metal, obtained by the reduction of the oxide in hydrogen, rapidly oxidises on exposure to the air, sometimes with incandescence. When heated in the air, it forms the oxide $Co_3O_4$. Cobalt decomposes steam at a red heat, yielding cobaltous oxide, CoO.

**Oxides of Cobalt.**—Three oxides of cobalt are recognised, namely, cobaltous oxide, CoO; cobaltic oxide, $Co_2O_3$; and cobalto-cobaltic oxide, $Co_3O_4$.

Four other oxides are known, which are regarded as compounds of the two first, having the composition $2CoO,Co_2O_3$; $3CoO,Co_2O_3$; $4CoO,Co_2O_3$; $6CoO,Co_2O_3$.

The monoxide, CoO, is basic, and yields the cobaltous salts. The sesquioxide, $Co_2O_3$, is feebly basic, forming only unstable salts. Stable double salts, however, corresponding to this oxide are known.

**Cobaltous Oxide** (*cobalt monoxide*), $CoO$, is formed when the sesquioxide is heated to redness in a stream of carbon dioxide, or gently heated in hydrogen. It is also obtained when the carbonate or hydroxide is heated in the absence of air. It forms a drab-coloured powder, which is unacted upon by the air, but when heated, forms $Co_3O_4$. When heated in either hydrogen or carbon monoxide, it is reduced to metallic cobalt.

**Cobaltous Hydroxide,** $Co(HO)_2$.—When potassium hydroxide is added to a solution of a cobaltous salt, a blue basic hydrate is precipitated, which, on boiling, is converted into the pink hydroxide $Co(HO)_2$. It turns brown on exposure to the air, by the absorption of oxygen. Both the oxide and hydroxide are really soluble in acids, giving cobaltous salts.

**Cobaltic Oxide** (*cobalt sesquioxide*), $Co_2O_3$, is obtained by carefully heating cobaltous nitrate until red fumes cease to be evolved. It is a dark grey powder, which, when strongly heated, is converted into the intermediate black oxide, $Co_3O_4$. Cobaltic oxide dissolves in cold acids, forming brown solutions, which contain unstable cobaltic salts. When warmed, these are converted into cobaltous salts, with evolution of oxygen in the case of oxy-salts, and of the halogen from haloid salts. This sesquioxide, therefore, behaves as a peroxide.

**Cobaltic Hydroxide,** $Co_2(HO)_6$, or $Co_2O_3,3H_2O$, is obtained as a nearly black precipitate, by the addition of an alkaline hypochlorite to a cobaltous salt. With acids it behaves as the oxide.

**Cobalto-Cobaltic Oxide,** $Co_3O_4$, is formed as a black powder, when the sesquioxide is strongly heated in air.

## COBALTOUS SALTS.

**Cobaltous Chloride,** $CoCl_2$.—When the carbonate, or any of the oxides, are dissolved in hydrochloric acid, the concentrated solution deposits dark red prisms (monosymmetric), having the composition $CoCl_2,6H_2O$. When exposed over sulphuric acid, they lose $4H_2O$, and are converted into a rose-red salt, $CoCl_2,2H_2O$, which reabsorbs moisture from the air to form the hexa-hydrate. When the di-hydrate is heated to about 100°, it is converted into violet-blue crystals of $CoCl_2,H_2O$; and at 120° it becomes anhydrous, and is blue. The blue salts, on exposure to the air, rapidly rehydrate themselves, and become pink.

Cobaltous chloride dissolves in alcohol, giving a deep blue solution, which, on the addition of water, also becomes pink. This property of forming pink hydrated salts, which become blue or green when nearly or quite anhydrous, is common to most cobaltous salts. Thus, the iodide $CoI_2,6H_2O$ forms rose-coloured crystals. When gently heated, it changes to a moss-green salt, $CoI_2,2H_2O$, which, when dehydrated, becomes nearly black.

**Cobaltous Sulphate,** $CoSO_4,7H_2O$, is obtained by dissolving the carbonate or oxides in sulphuric acid, and is deposited from the solution in dark red crystals, isomorphous with ferrous sulphate. Cobalt sulphate, like the sulphates of iron and nickel, forms double salts with alkaline sulphates, of which cobalt potassium sulphate, $CoSO_4,K_2SO_4,6H_2O$, is the best known.

**Cobaltic Salts.**—Single salts corresponding to cobalt sesquioxide are unstable, and exist only in solution. More stable double salts are known. Thus, when potassium nitrite is added to an acetic acid solution of cobalt chloride, a yellow crystalline precipitate is obtained, consisting of the double nitrite of cobalt and potassium—

$$2CoCl_2 + 10KNO_2 + 4HNO_2 = Co_2(NO_2)_6,6KNO_2 + \\ 2NO + 4KCl + 2H_2O.$$

The formation of this compound is made use of for separating cobalt from nickel, the latter element yielding no corresponding double nitrite. In the presence, however, of salts of barium, strontium, or calcium, nickel forms, with potassium nitrite, *triple* salts, such as $Ni(NO_2)_2,Ba(NO_2)_2,2KNO_2$, which are precipitated as yellow crystalline powders. Hence, in the presence of metals of the alkaline earths, nickel and cobalt cannot be separated by this method.

### SULPHIDES OF COBALT.

**Cobaltous Sulphide,** $CoS$, is obtained by heating cobaltous oxide with sulphur, or by fusing a mixture of cobalt sulphate, barium sulphide, and common salt. It forms bronze-coloured crystals, which are soluble in strong hydrochloric acid. Cobalt sulphide is precipitated as a black amorphous powder, when ammonium sulphide is added to a cobalt solution. The precipitate slowly dissolves in dilute mineral acids, but is insoluble in acetic acid. When heated in a stream of sulphuretted hydrogen, it yields the sesquisulphide $Co_2S_3$; and if mixed with sulphur, and heated in a current of hydrogen, it forms the disulphide $CoS_2$.

**Cobaltamines** (*ammoniacal cobalt compounds* *). Cobalt forms a large number of complex ammoniacal salts. A few of these contain the metal in the divalent condition, and are known as *ammonio-cobaltous salts;* but by far the larger number contain the hexavalent double atom $Co_2$, and are termed *ammonio-cobaltic compounds.* These compounds are classified as follows † :—

**Ammonio-Cobaltous Salts** are formed by the absorption of gaseous ammonia by anhydrous cobaltous salts, or by dissolving the salts in strong aqueous ammonia, with exclusion of air. In this way the following salts have been obtained—

Ammonio-cobaltous chloride, $CoCl_2,6NH_3$ { which, at 120°, is converted into $CoCl_2,2NH_3$.
Ammonio-cobaltous sulphate, $CoSO_4,6NH_3$.
Ammonio-cobaltous nitrate, $Co(NO_3)_2,6NH_3,2H_2O$.

**Ammonio-Cobaltic Salts.**—These may be arranged under the following classes and subdivisions:—

I. *Hexammonio Salts.*—General formula, $Co_2(NH_3)_6{\cdot}R_6$, where R equals a monacid radical, or its equivalent of *di* or *tri* acid radicals.

*Examples* { Hexammonio-cobaltic chloride (*dichro-cobaltic chloride*), $Co_2{\cdot}(NH_3)_6{\cdot}Cl_6,2H_2O$.
Hexammonio-cobaltic sulphate, $Co_2{\cdot}(NH_3)_6{\cdot}(SO_4)_3,6H_2O$.

II. *Octammonio Salts*—

(*a.*) *Praseo* ‡ *Salts.*—General formula, $Co_2{\cdot}(NH_3)_8{\cdot}R_6$.

*Examples* { Praseo-cobaltic chloride, $Co_2(NH_3)_8{\cdot}Cl_6,2H_2O$.
Praseo-cobaltic chloro-nitrate, $Co_2(NH_3)_8{\cdot}Cl_4{\cdot}(NO_3)_2,2H_2O$.

(*β.*) *Fusco Salts.*—General formula, $Co_2(NH_3)_8(HO)_2{\cdot}R_4$.

*Examples* { Fusco-cobaltic chloride, $Co_2(NH_3)_8(HO)_2{\cdot}Cl_4,2H_2O$.
Fusco-cobaltic sulphate, $Co_2(NH_3)_8(HO)_2{\cdot}(SO_4)_2,2H_2O$.

(*γ.*) *Croceo Salts.*—General formula, $Co_2(NH_3)_8(NO_2)_4{\cdot}R_2$.

*Examples* { Croceo-cobaltic chloride, $Co_2(NH_3)_8(NO_2)_4{\cdot}Cl_2$.
Croceo-cobaltic sulphate, $Co_2(NH_3)_8(NO_2)_4{\cdot}SO_4$.

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* For details respecting the preparation and properties of these salts, the student is referred to larger works.

† On the constitution of metallammonium compounds generally, see Werner, *Zeitschrift für Anorganische Chemie*, 1893, vol. iii.

‡ These names denote the characteristic colours of the salts; thus, *prasimus*, leek-green; *fuscus*, swarthy; *crocus*, yellow, &c.

III. *Decammonio Salts*—

(a.) *Roseo Salts.*—General formula, $Co_2(NH_3)_{10}(H_2O)_2R_6$.

*Examples*
- Roseo-cobaltic chloride, $Co_2(NH_3)_{10}(H_2O)_2Cl_6$.
- Roseo-cobaltic sulphate, $Co_2(NH_3)_{10}(H_2O)_2 \cdot (SO_4)_3 \cdot 3H_2O$.

(β.) *Purpureo Salts*—General formula, $Co_2(NH_3)_{10}X_2R_4$ (where X and R are either the same, or different acid radicals).

*Examples*
- Chloro-purpureo-cobaltic chloride, $Co_2(NH_3)_{10}Cl_2 \cdot Cl_4$.
- Chloro-purpureo-cobaltic sulphate, $Co_2(NH_3)_{10}Cl_2 \cdot (SO_4)_2$.
- Bromo-purpureo-cobaltic nitrate, $Co_2(NH_3)_{10}Br_2 \cdot (NO_3)_4$.

(γ.) *Xantho Salts.*—General formula, $Co_2(NH_3)_{10}(NO_2)_2 \cdot R_4$.

*Examples*
- Xantho-cobaltic chloride, $Co_2(NH_3)_{10}(NO_2)_2 \cdot Cl_4$.
- Xantho-cobaltic bromo-nitrate, $Co_2(NH_3)_{10}(NO_2)_2 \cdot Br_2 \cdot (NO_3)_2$.

IV. *Oxy-decammonio Salts.*—General formula, $Co_2(NH_3)_{10}R_4 \cdot X \cdot O(HO)$ (where X is either (HO) or an acid radical either the same as, or different from, R).

*Examples*
- Oxy-decammonio cobaltic chloride, $Co_2(NH_3)_{10}Cl_4 \cdot (HO) \cdot O \cdot (HO)$.
- Anhydro-oxy-decammonio cobalt chloride, $Co_2(NH_3)_{10}Cl_4 \cdot Cl_2 \cdot O \cdot (HO)$.

V. *Dodecammonio Salts* (luteo-cobaltic salts).—General formula, $Co_2(NH_3)_{12}R_6$.

*Examples*
- Luteo-cobaltic chloride, $Co_2(NH_3)_{12}Cl_6$.
- Luteo-cobaltic sulphate, $Co_2(NH_3)_{12}(SO_4)_3, 5H_2O$.

When cobalt compounds are fused with borax, a clear blue vitreous mass is obtained, which contains a borate of cobalt. A similar blue colour is imparted to ordinary potash glass, when a small quantity of a cobalt salt is added to the molten material, owing to the formation of a silicate of cobalt. Under the name of *smalt*, this substance has been manufactured for use as a pigment, by fusing the roasted cobalt ore with quartz sand and pearl-ash. The fused mass of deep blue glass is then finely ground beneath water.

## NICKEL.

Symbol, Ni. Molecular weight = 58.6.

**Occurrence.**—Nickel occurs chiefly in combination with arsenic as *kupfer nickel*,* $Ni_2As_2$; *white nickel*, $NiAs_2$; *nickel glance*, $Ni_2(AsS)_2$, also as *nickel blende*, NiS. Nickel ore almost invariably contains cobalt, and frequently antimony and bismuth.

**Modes of Formation.**—Nickel is obtained by reducing the oxide with carbon at a high temperature. It may be obtained as a black powder by reducing nickelous oxide in a stream of hydrogen, or by heating nickelous oxalate out of contact with air. It is also obtained as a lustrous coherent deposit by the electrolysis of an ammoniacal solution of the double sulphate of nickel and ammonia.

**Properties.**—Nickel is a lustrous white metal, with a faint yellow tinge when compared with silver. It is ductile and malleable, and at the same time very hard and tenaceous. It is susceptible of a very high polish. Nickel is attracted by the magnet, but loses this property when moderately heated. When obtained by reduction with charcoal, the metal contains a certain amount of carbon (like cast iron), which renders it less malleable; and when produced by reduction of the oxalate at a low temperature the powder is pyrophoric.

In the massive form, nickel is unacted upon by moderately dry air, but in moist air it tarnishes, and becomes covered with a film of nickelous oxide. It decomposes steam only slowly at a red heat, and is slowly attacked by dilute hydrochloric or sulphuric acid (contrast iron).

In a finely divided state, nickel absorbs carbon monoxide (see page 263).

Nickel is largely used for electro-plating iron and steel articles.

**Nickel Alloys.**—With copper, and with copper and zinc, nickel furnishes several important alloys. The small coinage in use in Belgium, Germany, and the United States, consists of 1 part of nickel and 3 parts of copper; while the so-called *German silver*, or *nickel-silver*, contains in addition about 1.5 parts of zinc.

---

* *Kupfer nickel* signifies *the false copper*, and was applied by the Germans in the middle ages to this ore, which resembled a copper ore, because they tried in vain to extract copper from it. It is probable that this ore had been smelted along with copper ores, under the belief that it contained copper, by the early ancients. Thus, a coin, 235 B.C., has been found to contain 20 per cent. of nickel.

**Oxides of Nickel.**—Three oxides of nickel have been obtained, namely, nickelous oxide, NiO; nickelic oxide, $Ni_2O_3$; and nickelo-[illegible]kelic oxide, $Ni_3O_4$. The first alone is basic.

**[illegible]ckelous Oxide** (*nickel monoxide*), NiO, is obtained as a [illegible]enish powder by heating nickel carbonate, or hydroxide, out of [illegible]ntact with air. [illegible] acids yielding nickel salts. [illegible]hen heated in h[illegible] monoxide, it is readily re- [illegible] the metall[illegible]

**[illegible]ous Hy[illegible]** is obtained as a pale green [illegible]e when [illegible] is added to a solution of a [illegible] salt: the precipitat[illegible] composition $4Ni(HO)_2,H_2O$. [illegible]en strongly heated it is c[illegible]d into nickelous oxide and water. It is readily soluble in a[illegible]orming the nickel salts; and it also dissolves in ammonia and in solutions of ammonium salts.

**Nickel Sesquioxide,** $Ni_2O_3$, is obtained as a black powder when the nitrate is decomposed by heat at the lowest temperature. With hydrochloric acid and sulphuric acid it behaves like a peroxide; yielding nickel salts, with the elimination of chlorine and oxygen respectively—

$$Ni_2O_3 + 6HCl = 2NiCl_2 + 3H_2O + Cl_2.$$
$$Ni_2O_3 + 2H_2SO_4 = 2NiSO_4 + 2H_2O + O.$$

It is soluble in ammonia, with evolution of nitrogen—

$$2Ni_2O_3 + 2NH_3 = 6Ni(HO)_2 + 3H_2O + N_2.$$

**Hydrated Sesquioxide of Nickel,** $Ni_2(HO)_6$, or $Ni_2O_3,3H_2O$. When chlorine is passed through water, or sodium hydroxide, in which nickelous hydroxide, $Ni(HO)_2$, is suspended, a black powder is obtained having the composition $Ni_2O_3,3H_2O$. The same compound is obtained when a nickel salt is added to a solution of bleaching-powder. In contact with acids and ammonia it behaves like the oxide.

**Nickelo-nickelic Oxide,** $Ni_3O_4$, is obtained as a grey metallic-looking mass, when nickel chloride is heated to about 400° in a stream of oxygen.

**Nickel Salts.**—Nickel forms only one series of salts, corresponding to the monoxide. In the anhydrous state these are usually yellowish, while in the hydrated condition they are green.

**Nickel Chloride,** $NiCl_2$, is obtained as a yellow amorphous mass, by dissolving the oxide or carbonate in hydrochloric acid, and evaporating the solution to dryness. When heated in a current of chlorine it sublimes in the form of lustrous golden yellow scales, which dissolve in water forming a green solution. From the aqueous solution, green crystals of the composition $NiCl_2,6H_2O$ are deposited.

Anhydrous nickel chloride absorbs gaseous ammonia forming the compound $NiCl_2,6NH_3$, which when deposited from an aqueous solution, forms blue octahedrons.

**Nickel Sulphate,** $NiSO_4,7H_2O$, is produced when the metal, the carbonate, or the oxide is dissolved in dilute sulphuric acid, and the concentrated solution is allowed to crystallise at the ordinary temperature. It forms green crystals, isomorphous with magnesium sulphate. When heated to 100° the crystals lose $6H_2O$, and above 300° the salt becomes anhydrous. The anhydrous salt absorbs gaseous ammonia, being converted into a pale violet powder having the composition $NiSO_4,6NH_3$. When nickel sulphate is dissolved in strong aqueous ammonia, the solution deposits dark blue quadratic crystals of $NiSO_4,4NH_3,2H_2O$.

With sulphates of the alkalies, nickel sulphate forms double salts, of which the ammonium salt is the most important, $NiSO_4,(NH_4)_2SO_4,6H_2O$. It is obtained by mixing concentrated solutions of the two sulphates in the requisite proportions. This salt is employed in the process of nickel-plating.

**Nickelous Sulphide** (*nickel monosulphide*), $NiS$, occurs as the mineral *capillary pyrites*. It is obtained as a bronze-like mass, insoluble in hydrochloric acid, by heating sulphur and nickel together. In the hydrated condition, nickel sulphide is precipitated as an amorphous black powder, on the addition of ammonium sulphide to a nickel salt. The precipitate is scarcely soluble in hydrochloric acid, but partially dissolves in excess of ammonium sulphide forming a brown solution. Three other sulphides have been obtained, having the composition $Ni_2S$, $NiS_2$, and $Ni_3S_4$.

# CHAPTER XIV

## *THE TRANSITIONAL ELEMENTS OF THE SECOND AND FOURTH LONG PERIOD*

***Ruthenium***, Ru = 103.5. ***Rhodium***, Rh = 104.1. Palladium, 106.2.
***Osmium***, Os = 191. Iridium, Ir = 192.5. Platinum, 194.3.

THESE elements, although constituting *two* transitional groups, are very closely related to each other. In nature they all occur associated together in what is commonly known as *platinum ore*, and they are on this account usually spoken of as *the platinum metals*.

*Platinum Ore*, or *native platinum*, contains all these elements in the metallic state. It is found in small grains, sometimes in nuggets, in alluvial deposits and river sand, principally in Brazil, Borneo, California, Australia, and the Urals. Native platinum contains from 60 to 86 per cent. of platinum, the remainder consisting of the other five metals of the group, together with varying quantities of gold, copper, and iron. Amongst the grains of platinum ore, there are also found grains which consist essentially of an alloy of platinum and iridium (containing from 30 to 75 per cent. of iridium) known as *platin-iridium:* and also particles of an alloy of osmium and iridium (called *osmiridium*), which contain from 30 to 40 per cent. of osmium, as well as small quantities of rhodium and ruthenium.

They are all white lustrous metals, having high melting-points. They are unacted upon by air or oxygen at ordinary temperatures; and, with the exception of osmium (which burns when strongly heated, forming the tetroxide), they are scarcely oxidised by oxygen at any temperature.

With the exception of palladium, which readily dissolves in hot nitric acid, these metals are unacted upon by ordinary acids. Aqua regia converts osmium into the tetroxide; it dissolves platinum with formation of the tetrachloride, and slowly acts upon ruthenium, but is without action upon rhodium and iridium.

The specific gravities of the metals of the first group, although very close to one another, are widely different from those of the second group; and it will be seen that the specific gravities fall, with increasing atomic weights, thus—

Ru, sp. gr. = 12.26. Rh, sp. gr. = 12.1. Pd, sp. gr. = 11.4.
Os, ,, = 22.47. Ir, ,, = 22.38. Pt, ,, = 21.5.

The element osmium is the heaviest known substance.

The most easily fusible of these metals is palladium, which melts about the temperature of wrought iron. The melting-point of platinum is somewhat higher, but it may be boiled by the oxyhydrogen flame. Rhodium and iridium come next in order of fusibility, the latter metal being just fusible by the oxyhydrogen flame, while ruthenium has a still higher melting-point. Osmium has not been melted. When heated to the melting-point of iridium, osmium volatilises; and if air be present, it burns.

The following oxides of these metals are known—

| | | | | | |
|---|---|---|---|---|---|
| — | — | — | — | $Pd_2O$ | — |
| RuO | OsO | RhO | — | PdO | PtO |
| $Ru_2O_3$ | $Os_2O_3$ | $Rh_2O_3$ | $Ir_2O_3$ | — | — |
| $RuO_2$ | $OsO_2$ | $RhO_2$ | $IrO_2$ | $PdO_2$ | $PtO_2$ |
| $RuO_4$ | $OsO_4$ | — | — | — | — |

Ruthenium, osmium, rhodium, and iridium form salts corresponding to the sesquioxide, such as ruthenious chloride, $Ru_2Cl_6$; rhodium sulphate, $Rh_2(SO_4)_3$; iridious chloride, $Ir_2Cl_6$.

With the exception of rhodium, they all form chlorides, corresponding to the dioxides, thus—ruthenic chloride, $RuCl_4$; iridic chloride, $IrCl_4$; platinic chloride, $PtCl_4$, while palladium and platinum yield pallad*ous* and palatin*ous* compounds, corresponding to their monoxides.

The tetroxides of ruthenium and osmium are remarkable in melting at an extremely low temperature (about 40°), and boiling about 100°. They yield intensely irritating vapours, which, in the case of osmium tetroxide, exerts a most injurious effect upon the eyes, and is extremely poisonous. (Osmium tetroxide is commonly known as *osmic acid.*) Osmium and ruthenium also exhibit a non-metallic character in forming compounds derived from the unknown ruthenic and osmic trioxides, such as potassium ruthenate, $K_2RuO_4$, and potassium osmate, $K_2OsO_4$ (the corresponding ruthenic and osmic acids are unknown). Ruthenium also forms potassium per-ruthenate, $KRuO_4$ (analagous to permanganate), although the corresponding acid and peroxide, $Ru_2O_7$, are unknown. The most important of these elements is platinum.

## PLATINUM.

Symbol, Pt. Molecular weight = 194.3.

In order to separate platinum from the other metals with which the *native platinum* (see page 642) is mixed, the ore is digested in dilute aqua regia, under slightly increased pressure. The solution so obtained contains the higher chlorides of platinum, palladium, rhodium and iridium (for although in the pure state the last two named metals are scarcely attacked by aqua regia, when alloyed with much platinum they dissolve). The solution is evaporated to dryness, and heated to 125°, whereby the palladium and rhodium are obtained in the form of their lower chlorides, $PdCl_2$ and $Rh_2Cl_6$ (the latter of which, in the anhydrous condition, is insoluble in water). The residue is extracted with water, and to the clear solution, acidified with hydrochloric acid, ammonium chloride is added. The double chloride of platinum and ammonium ($PtCl_4,2NH_4Cl$), separates out as yellow crystals, while the corresponding iridium salt, being more soluble, remains for the most part in solution, and may be obtained by concentrating the mother liquor. The ammonium platinic chloride, on being ignited, loses ammonium chloride and chlorine, leaving the metal in the form of a black spongy mass known as *spongy platinum*, which is then melted by means of the oxyhydrogen flame in a lime crucible. The platinum so obtained, usually contains small quantities of iridium, and traces of associated metals.

Pure platinum is obtained by alloying commercial platinum with pure lead, and treating the alloy first with nitric acid, which dissolves any copper and iron, a part of the palladium and rhodium, and most of the lead; and then with dilute aqua regia, which dissolves the whole of the platinum and the remaining lead, with traces of rhodium. From this solution the lead is precipitated as sulphate, and the platinum is then precipitated as the double chloride, by ammonium chloride. To remove traces of rhodium which are present, the dried double chloride is ignited with hydrogen potassium sulphate, whereby the rhodium is converted into a soluble double sulphate of rhodium and potassium, while the platinum is reduced to the condition of the spongy metal.

**Properties.**—Platinum is a lustrous, greyish-white, malleable, and ductile metal. At a red heat it may be welded with great ease. It is melted by the oxyhydrogen flame, and vessels of platinum are readily made by fusing the metal together in this way. Heated platinum absorbs large quantities of hydrogen (see page 157); and when the metal is melted in the oxyhydrogen flame, it exhibits the phenomenon of "spitting," when it again solidifies (see Silver, page 518). Platinum does not combine with oxygen at any temperature, neither does the heated metal absorb this gas; but it has the property, when cold, of condensing oxygen upon its surface. A piece of clean platinum foil or wire, when introduced into a mixture of oxygen, and a readily inflammable gas or vapour (such as hydrogen, ether, alcohol, &c.), causes their combination; and occasionally the metal becomes red hot, and ignites the mixture. This action is more rapid in the case of platinum sponge, when a larger surface is brought into play, and a fragment of this material introduced into a detonating mixture of oxygen and hydrogen at once determines its explosion.

Platinum is not acted upon by either nitric or hydrochloric acid. It is oxidised when fused with caustic alkalies, or with potassium nitrate, and is also attacked by fused alkaline cyanides. In the form of sponge, it is dissolved by boiling potassium cyanide with the evolution of hydrogen, and formation of a double cyanide.

Platinum readily combines with phosphorus, silicon, and carbon. The carbide of platinum is formed when the metal is continuously heated by a smoky flame, or one in which combustion is incomplete, hence care is necessary in the use of platinum vessels.

**Platinum Black** is the name given to the finely-divided metal obtained by precipitating platinum from its solutions by reducing agents, or by metals. It is a soft, black powder, which is capable of absorbing, or condensing upon its surface, large quantities of oxygen. It therefore acts as a powerful oxidising agent.

**Platinum Alloys.**—Platinum readily alloys with many metals; hence compounds of easily reducible metals should not be heated in vessels of platinum. The most important alloys are those with iridium. The addition of 2 per cent. of iridium is found greatly to increase the hardness, and raise the melting-point of platinum. An alloy containing 10 per cent. of iridium resists the corrosive action of chemical reagents to a greater extent than pure platinum (see Fluorine, page 310).

**Oxides of Platinum.**—Platinous oxide, $PtO$, and platinic oxide, $PtO_2$, are obtained in the form of dark grey or black powders, by gently heating the corresponding hydroxides. When strongly heated they are converted into the metal.

**Platinous Hydroxide,** $Pt(HO)_2$, is obtained by the action of potassium hydroxide upon platinum dichloride. It is a black powder, which dissolves in the halogen acids, yielding platin*ous* compounds.

**Platinic Hydroxide,** $Pt(HO)_4$. is prepared by adding boiling potassium hydroxide to a solution of platinum tetrachloride, and treating the precipitate with acetic acid to remove the potash. When dried it forms a yellowish powder, which is soluble in acids to form platinic salts. Platinic hydroxide behaves both as a weak base, and a feeble acid. With stronger bases it forms compounds known as *platinates*, which are yellow crystalline salts. The sodium salt has the composition $Na_2O,3PtO_2,6H_2O$.

**Platinum Dichloride** (*platinous chloride*), $PtCl_2$, is produced when platinum tetrachloride is heated to about 250°. It forms a greenish powder, insoluble in water. It dissolves in hydrochloric acid, giving a reddish-brown solution which is believed to contain the double compound $PtCl_2,2HCl$, or $H_2PtCl_4$, to which the name *chloro-platinous acid* has been given: the compound has never been isolated, but a number of double salts of platinous chloride with other chlorides are known, which may be regarded as derivatives of this acid, and which are therefore termed chloroplatinites; thus, potassium platinous chloride, $2KCl,PtCl_2$, or potassium chloro-platinite, $K_2PtCl_4$, is obtained as fine red crystals, by adding potassium chloride to a solution of platinous chloride in hydrochloric acid. This salt is used in the *platinotype* photographic process.

**Platinum Tetrachloride** (*platinic chloride*), $PtCl_4$, is obtained by dissolving the metal in aqua regia, and removing the excess of the acids by evaporating to dryness and gently heating the residue. From its aqueous solution, the salt deposits in large red crystals having the composition $PtCl_4,5H_2O$, which are not deliquescent. When the salt is crystallised from a hydrochloric acid solution, or when the aqua regia solution is evaporated to expel the nitric acid, with frequent addition of hydrochloric acid, the double compound of platinic chloride and hydrochloric acid is formed, $PtCl_4,2HCl$, which is deposited as reddish-brown deliquescent crystals, with $6H_2O$. To this substance (which is commonly called platinic chloride), the name *chloro-platinic acid* has been given, and the double salts of platinic chloride and various chlorides are regarded as salts of this acid. The most important of these chloro-platinates are those of the alkali metals, their different solubilities being made the basis for the separation of these metals.

**Potassium Chloro-platinate** (or *potassium platinic chloride*), $2KCl,PtCl_4$ or $K_2PtCl_6$, is obtained as a yellow crystalline precipitate, by adding potassium chloride to platinic chloride. It is soluble in 100 parts of water at the ordinary temperature to the extent of 1.1 parts, and at 100°, 5.18 parts. It is insoluble in alcohol.

The rubidium and caesium compounds are very similar, but are still less soluble in water, 100 parts of water at 20° dissolving 0.141 of the rubidium and 0.07 of the caesium salt.

**Ammonium Chloro-platinate**, $2NH_4Cl,PtCl_4$, closely resembles the potassium salt, being slightly less soluble, but more so than the rubidium compound.

**Sodium Chloro-platinate**, $2NaCl,PtCl_4,6H_2O$, is a reddish-yellow salt, readily soluble in both water and alcohol.

**Platino-cyanides.**—Just as platinous chloride combines with metallic chlorides to form chloro-platinites, so platinous cyanide, $Pt(CN)_2$, unites with other cyanides, forming similarly constituted double compounds, known as platino-cyanides.*

Potassium platino-cyanide, $K_2Pt(CN)_4$, or $2KCN,Pt(CN)_2$, is formed when spongy platinum is dissolved in boiling potassium cyanide. The platino-cyanides may be regarded as the salts of platino-cyanic acid, $H_2Pt(CN)_4$. Both the acid and the salts are characterised by the wonderful play of colours they exhibit, when viewed in different lights; and by forming different coloured crystals with varying quantities of water of crystallisation (see page 192).

**Sulphides of Platinum.**—Platinous sulphide, PtS, and platinic sulphide, $PtS_2$, are obtained as amorphous black powders by the action of sulphuretted hydrogen upon the respective chlorides.

**Oxysalts of Platinum.**—Few well defined single salts of platinum with oxyacids are known. This element, however, exhibits a great tendency to form complex double salts. One such series of compounds is seen in the *platino-nitrites*, which may be regarded as the salts of platino-nitrous acid, $H_2Pt(NO_2)_4$.

These salts are remarkable, in that the platinum they contain cannot be detected by the ordinary tests for that metal; just as the iron present in ferro-cyanides is not detected by the ordinary reagents used in testing for that metal.

**Ammoniacal Platinum Bases, or Platinamines.**

Like cobalt, platinum forms a large number of basic compounds with ammonia, many of which are of extremely complex composition. The first of these to be discovered was a bright green salt, obtained by the action of ammonia upon platinous chloride, having the composition $PtCl_2,2NH_3$, or $Pt(NH_3)_2Cl_2$, and known as *the green salt of Magnus.* Many of the platinamines exhibit isomerism; thus, a compound known as the *chloride of Reiset's second base* is a yellow crystalline salt having the same composition as Magnus's green salt. Twelve distinct series of ammoniacal platinum compounds are known, four of which are derived from platin*ous* and the remainder from platin*ic* salts; the former are termed *platoso* ammonia compounds, while the latter are distinguished as the *platino* compounds.†

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* The name Cyano-platinites might with advantage be applied to these compounds.

† For detailed descriptions of these compounds, the student is referred to larger works on chemistry: and on the constitution of these, and metallammonium compounds generally, the article by Werner, in the *Zeitschrift für Anorganische Chemie*, 1893, vol. iii. p. 267, may be consulted.

# NOTE

## *A NEW GASEOUS CONSTITUENT OF THE ATMOSPHERE*

In making accurate determinations of the densities of gases, it has been found by Lord Rayleigh that atmospheric nitrogen always gives a somewhat higher number than that obtained for nitrogen which is prepared from chemical compounds.

While this book was going through the press, Lord Rayleigh and Professor Ramsay have announced the discovery of a new gaseous constituent of the atmosphere.*

They have succeeded in isolating from so-called "atmospheric nitrogen" another gas, resembling nitrogen in its inertness, but having a higher density. They have obtained this gas by passing "atmospheric nitrogen" over heated magnesium, whereby the true nitrogen was absorbed, and a residual gas (amounting to about 1 per cent. of the original "atmospheric nitrogen") was obtained, whose density was found to be 19.09.

Whether this gas is a compound, or a new elementary body, has yet to be discovered.

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* British Association, August 1894.

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